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COMPREHENSIVE REVIEW OF SEWAGE CHLORINATION

Ralph W. Buelow, et al

Northeast Marine Health Sciences Laboratory
Narragansett, Rhode Island

July 1967

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Water Supply and Sea Resources Program

COMPREHENSIVE REVIEW OF SEWAGE CHLORINATION

by

Ralph W. Buelow and
Pearce M. Klazer

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NORTHEAST MARINE HEALTH SCIENCES LABORATORY
Narragansett, Rhode Island 02882

July 1967

FOREWORD

The National Shellfish Sanitation Program, which is an intimate part of the Water Supply and Sea Resources Program, has been concerned with all factors pertaining to protecting the public health from adverse affects of eating shellfish harvested from polluted areas. Among these factors are the proper design and construction of sewage treatment plants. Although the Program does not design or offer funds for construction, it has in recent years offered consultation services to various state and federal agencies.

One of the most important facets of sewage treatment is disinfection of the waste. Sole reliance has been placed on chlorination for destruction of pathogens, since other unit operations are not expected to sufficiently kill them. During the review of proposed projects chlorination equipment, its installation, and operation has received quite a bit of attention. Because of this reason, this report has been written as part of the duties of the National Shellfish Sanitation Program.

This report is intended to be as comprehensive as is reasonably possible in light of the rapidly changing technology. It may be considered preliminary to more field and research work on effects of chlorination on various pathogens, and the accompanying need to modify equipment to meet the requirements of public health protection. Although the original intent of this report was aimed at a raw food product, oysters, clams and mussels, the nature of the subject causes it to cover points applicable to water supply and recreation as well.

INTRODUCTION

Disinfection of sewage is of primary concern to shellfish sanitation. The use of chlorine and its compounds is practically the only means used for sewage disinfection and therefore many in shellfish sanitation should be familiar with chlorination practices. We have attempted to combine the important aspects of sewage chlorination as found in the published literature in order to eliminate the necessity of searching out the references by the reader. The subject material is applicable to design, construction, and modification of the important factors of chlorination in considerably more detail than generally found in a sewage treatment plant design manual.

It is hoped that this work can be utilized by personnel reviewing sewage treatment plant construction plans as well as those inspecting plant operation in connection with growing area sanitary surveys.

The importance of chlorination in relation to conditionally approved growing areas requires an understanding of chlorination practices both good and poor, existing and possible along with reccommended corrective measures.

We are continuing investigative work toward improving chlorination practices and will supplement this work as material becomes available. The parts of this work that will be most likely supplemented are those dealing with the assurance of satisfactory disinfection which includes chlorine residual control, contact tank effectiveness, and the meager section dealing with "Effects of Chlorination on Estuaries."

This report contains names of manufacturers products and refers to manufacturers publications in numerous places. This is not to be construed as an endorsement but rather a use of the best material available.

ACKNOWLEDGMENTS

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CHLORINE AND ITS COMPOUNDS

Liquid Chlorine

The most widely used method of chlorination of sewage (and water supplies) involves compressed chlorine gas or liquid chlorine. Liquid chlorine, usually manufactured from electrolysis of brine solutions is delivered to sewage treatment plants in metal tanks, and by means of certain dispensing equipment, is vaporized and fed to the sewage in a solution. A description of the manufacture of liquid chlorine and the various impurities are given in Appendix B. The impurities directly or indirectly affect all equipment involved. Chlorine must be 99.5% pure by volume according to Federal Specification BB-C-120 and AWWA Specification B301-59.

Appendix A gives a brief history of chlorine and some elementary chlorine chemistry and its development as a disinfectant.

The merits of liquid chlorine develop throughout the report as it progresses from equipment to application at the sewage treatment plant.

Chlorine Compounds

Recent years have shown an increasing interest by sanitary engineers in chlorine compounds for disinfection. These compounds usually are delivered in powder or flake form and are put into solution which is fed to the sewage.

Table 1 lists several of the compounds and certain features for shipping and handling. Calcium or sodium hypochlorites are used more than the others.

TABLE 1 CHLORINE COMPOUNDS USED FOR DISINFECTION*

Chemical Name	Formula	Trade Name	Shipping Containers	Handling Materials	Available Forms	Commercial Strength	Character
Ammonium Chloride	NH_4CL	Sal ammoniac	100# kegs, 212-550# bbls., 880-1200# hoghds.	iron or rubber	white lump, crystal	-	hygroscopic, volatilizes
Calcium Hypochlorite	$Ca(OCl)_2 \cdot 4H_2O$	HTH, Pit-Tabs, Perchloron, Pittchlor, Chlor-Tabs	3-3/4, 5#, 7½, 15# cans, 100, 300, 800# drums, 415# bbls.	glass, rubber, stoneware, wood	white grannual powder	70% available Cl_2	1-3% available Cl_2 solution used
Chlorinated Lime	$CaO \cdot 2CaOCl_2 \cdot 3H_2O$	Bleaching Powder, Chloride of Lime	100, 300, 800# drums	glass, rubber, stoneware, wood	white powder	25-37% available Cl_2	deteriorates, hygroscopic
Chlorine Dioxide	ClO_2	Chlorine Dioxide	generated as used	plastics, soft rubber, (avoid hard rubber)	yellow-red gas	26.3% available Cl_2	
Sodium Chlorite	$NaClO_2$	Technical Sodium Chlorite	100# drums	metals (avoid cellulose)	light-organge powder, flake	30% available Cl_2	generates ClO_2 at PH 3.0
Sodium Hypochlorite	$NaOCl$	Sodium Hypochlorite	5, 13 gal. carboys, 1300-2000 gal. tank trucks	ceramics, glass, plastics, rubber	light-yellow liquid	12-15% available Cl_2	deteriorates

*Derived from Reference No. 7

Selection of Type of Chlorine

The effectiveness of the two types of chlorination -- liquid and compounds -- are the same, since the chemical principles of disinfection are the same. The choice depends on a) economics as it relates to equipment, b) safety -- liquid chlorine is more hazardous, c) relative cost per percentage kill of pathogenic organisms, and d) availability.

Each has its advantages and disadvantages for each of these four decision constraints.

GENERAL EQUIPMENT AND OPERATION

Liquid Chlorine

Containers. Liquid chlorine is produced in this country at about 70 plants and can be purchased from about the same number of "repackagers." A repackager is the chlorine dealer who purchases bulk quantities of chlorine from the producer and sells it in smaller containers to local customers. Liquid chlorine is available in several types of steel containers, each of which is registered with the Bureau of Explosives and is constructed in compliance with Interstate Commerce Commission or Coast Guard regulations. Chlorine can be purchased in small lecture bottles but more commonly in cylinders containing 100, 105, or 150 pounds of the liquid. These cylinders, commonly used at small sewage plants, are designed to stand on end and all are less than 6 feet tall. The operating valve is located on top of the cylinder, beneath a screw-on protective cap. All valves are equipped with a plug designed to melt and release internal pressure between 158-165°F. Chlorine is nonflammable, but chlorine containers subjected to excessive heat have been known to explode, Chlorine Institute (1959b).

All chlorine containers must be routinely checked as specified by ICC regulations. Chlorine cylinders, for example, must be hydrostatically pressure checked every 5 years to pressure limits specified by the ICC. The date of last testing should be clearly indicated on the side of the chlorine container. The maximum amount of liquid chlorine placed in a container is also regulated, and that amount cannot exceed a density of 1.25 (the ratio, by weight, of chlorine in the container to the weight of water that the container will hold). At room temperature, the chlorine repackager or producer should allow some space in the container (over 10%) for liquid expansion such that a properly filled container will be completely filled with liquid chlorine at 158°F.

Chlorine is also sold in containers holding about a ton of the liquid. The container is designed such that at one end there are two operating valves for discharging either gaseous or liquid chlorine. These valves are protected in transit and storage by a protective hood which is detached when the container is filled or evacuated. The ton container is also equipped with safety plugs designed to melt and relieve internal pressure at elevated temperatures. The ton container has six such plugs, three on each end. The ton containers can be ordered as single units or up to multi-unit railroad cars (TMU cars) containing 15 one-ton containers.

The ICC allows liquid chlorine to be transported in specially designed railroad tank cars of 16-, 30-, and 55-ton capacities. The tank cars are equipped to discharge liquid chlorine from the tank dome through one of two valves, each containing a device to shut off excessive flow such as in the case of a broken discharge line. The tank car has two other operating valves designed to draw off gaseous chlorine, however, these latter valves are not commonly used. A spring-loaded safety valve is also included in the dome to relieve internal pressure.

Though rarely used by sewage plants, chlorine can also be ordered in 15-16 ton tank trucks or 550-1,110 ton barges. These methods of chlorine transport usually require the receiver to provide chlorine storage facilities for rapid chlorine transfer.

Recommendations as to what type of container to purchase are given in the ASCE-Manual of Engineering Practice No. 36, ASCE (1963).

Table 2 gives dimensions and weights of common containers.

Table 3 presents scope of container size versus daily use by a sewage treatment plant.

TABLE 2 DIMENSIONS AND WEIGHTS OF COMMON CHLORINE CONTAINERS

After Laubusch (1963)

Container	Capacity Lbs.	Weight Empty, Lbs.	Length	Overall Height	Diameter Inches
Cylinders	100	80-115(1)	-	53"-59"(2)	8-1/4-8-1/2
	100	63- 79(1)	-	53"-55"(2)	8-1/4-8-1/2
	100	95-105(1)	-	40"-43"(2)	10-1/2-10-3/4
	100	63- 76(1)	-	39-3/4"-43"(2)	10-1/2-10-3/4
	105	85(1)	-	41-1/8"(2)	10-1/4-10-1/2
	105	72- 77(1)	-	40"-41"(2)	10-1/4-10-1/2
	105	72- 77(1)	-	57"-58"(2)	8-1/4-8-1/2
	150	120-140(1)	-	52"-56"(2)	10-1/2-10-3/4
	150	65-105(1)	-	53"-56"(2)	10-1/4-10-3/4
Ton Container	1-ton	1,300-1,650(1)	79-3/4"-82-1/2"(2)	-	30
TMU	15-ton	54,500-59,000(3)	42'4"-47'0"(4)	6'8"-7'6"(5)	9'6"-10'1"(6)
Rail Tank Car	16-ton	42,000-51,000	32'2"-33'3"(4)	10'5"-12'0"(5)	9'2"-9'6-1/2"(6)
	30-ton	55,000-65,000	33'10"-35'11-1/2"(4)	12'4-1/2"-13'7"(5)	9'3"-9'10"(6)
	55-ton	76,000-84,000	38'1-1/2"-43'0"(4)	14'3"-14'10-1/2"(5)	9'3"-10'7-1/2"(6)

(1) Weight includes protection hood and valves.

(2) Height to top of valve protection hood; height to center line of valve outlet is about 3-1/2" less.

(3) Weight for car with empty containers.

(4) Length over strikers.

(5) Height for empty car and is measured from top of rail. Heights of loaded cars may be as much as 4" less.

(6) Extreme width.

TABLE 3

Daily Chlorine Usage	Container*
up to 300#	150#
up to 2,000#	Ton
over 2,000#	Tank Car

---

*Local availability of chlorine and the policy of the supplier may govern the choice of container size.

Transportation. Chlorine is nearly always shipped as a liquid. Interstate shipment of chlorine is regulated by either the Interstate Commerce Commission or the Coast Guard depending upon the mode of transportation. Intrastate shipments are subject to state regulations, however, "In practice chlorine shippers do not differentiate between inter- and intra-state shipments," Chlorine Institute (1959). Besides designating periodic pressure testing and inspection of containers, ICC regulations also prohibit a) gases or liquids other than chlorine to be introduced into a shipping container (other than during testing), b) shipping of leaking chlorine containers or those exposed to fire, c) shipping a chlorine container loaded without the permission of the owner, and d) receiving broken, leaky, or defective containers without informing the Bureau of Explosives of the Association of American Railroad. This agency acts as an enforcing group of the ICC regulations. The ICC regulations are quite numerous and are only mentioned to inform the reader that interstate chlorine shipment is under strict control.

Chlorine cylinders can be shipped in any amount by rail or truck but are generally transported to the sewage plant by truck, Laubusch (1959b).

Ton containers can be hauled by truck if they are properly secured and if an adequate container transfer device is available on the truck in case of an emergency during transit, Laubusch (1963). The ton containers can be transported by rail only in multi-unit cars (TMU) designed to carry 15 containers. The TMU cars are usually unloaded at the purchaser's facility and empty containers are loaded on the same car for return. Since the transportation fee for the car is a set rate, it is not recommended to order less than 15 containers on the TMU car. Railway tank cars are trip leased and are most economical only at the larger sewage plants. Since chlorine storage facilities present numerous difficulties, chlorine is customarily used directly from the tank car.

Receiving and Handling. Rules and regulations, made to correct for lack of knowledge aptly apply to chlorine handling. The chlorine handler must remember that chlorine containers whether full or partially full at normal temperatures will be under pressure and the contents which are potentially harmful as well as corrosive in character will escape if the opportunity presents itself. Since the containers are not indestructible, their handling deserves care, caution, and common sense. They should not be dropped and receiving facilities should be designed to limit the risk of dropping. The hoisting of chlorine cylinders should be avoided if at all possible. If they must be lifted, those techniques that will ensure safe transit should be employed -- "Chains, lifting magnets and rope slings which encircle the cylinders are unsafe," according to Laubusch (1963). Although skids, troughs, upending cradles, etc., have been used, a satisfactory method is to haul the cylinder on a hand truck. While being moved, the cylinder is fastened to the hand car by a clasp or chain two-thirds the way up the cylinder. Cylinders are never to be lifted by the protective cap. This cap is designed only to protect the operating valve, and it should be removed only when the cylinder is in use.

Handling precautions observed for cylinders apply equally to ton containers. Since the gross weight of a full ton container can reach up to 3,650 pounds, the use of an unloading and transporting device other than a hand car is necessary. Unloading ton containers requires the use of a hoist of at least a 2-ton capacity and of sufficient height to lift the container completely out of the hauling vehicle and over any stored containers and other objects without the danger of impact. Since the ton containers are customarily hauled with the longitudinal axis horizontal, they are easily grasped using lifting clamps or hooks secured at each end. Once the container is transferred from the shipping vehicle, it can be transported to storage either by an overhead monorail or possibly by rolling it manually on rails.

With the use of larger chlorine containers, stricter regulations apply. Use of TMU railroad cars, for example, requires a private siding for unloading. If none exists, then the car can be unloaded on the carrier tracks, with the permission of the delivery carrier, and from there the containers can be shipped by motor truck. Since the TMU car handrails cannot be removed, the chlorine container hoisting device must be capable of lifting the containers over them. Sewage plant operators, as well as designers, should be aware of the ICC regulations in employment of the TMU car as well as the recommendations set forth by the Chlorine Institute, Inc. The Chlorine Manual, published by the

Chlorine Institute, is a useful reference for chlorine transport, handling, and safety recommendations for those seeking a more specific picture of the subject than discussed here.

Regulations for unloading railroad tank cars are even more extensive. ICC regulations require that tank cars containing liquid chlorine can only be unloaded on private tracks, the unloading must be done only by qualified personnel, and during the unloading period the car must be attended. The tank car brakes must be set and the wheels blocked and prescribed warning signs must be placed about the car. Connections must be properly attached before the discharge valves are opened and they must be detached when the car is unloaded or when unloading is discontinued. All equipment, including tools, used must be free from oil, dirt, and grit. Precautions specified by the Chlorine Institute above and beyond the ICC regulations are recommended. Where tank cars are to be employed, the designer should consider two siding tracks to avoid chlorine disruption during tank car changeover, or some other means of quaranteeing a continuous supply.

Storage and Safety. Recommendations for chlorine storage, whether it be in cylinders or ton containers take into account three characteristics of chlorine: chlorine gas is heavier than air, chlorine can be highly reactive, and internal pressure of chlorine containers increases with increasing temperature. However, chlorine storage recommendations are not only limited to safety but also convenience.

At normal room temperatures, liquid chlorine is about 1½ times heavier than water. One unit volume of the liquid at these temperatures rapidly vaporizes into about 450 unit volumes of the gas. Since free chlorine is about 2½ times heavier than air, it will seek the lowest levels. For this reason, container storage areas should not be in low elevation rooms, areas from which the gas cannot be safely and easily evacuated. The storage area obviously should be well ventilated, Chlorine Institute (1959b). Wallace and Tiernan, Inc. recommends a complete air changeover in storage rooms under normal conditions of about once every 15 minutes, and in the case of container leakage, once every 3 to 4 minutes. A circulation fan can be used with an air inlet located near the floor level. The fan switch should be located outside the storage area.

The potential reactivity of liquid or gaseous chlorine is another problem to consider in storing containers. Chlorine in combination with water is highly corrosive. For this reason it is recommended that any container leaks should never be wetted as this will only increase the leakage. Chlorine is highly reactive with organic compounds such as turpentine, ether, anhydrous ammonia, and fine metal particles (Ibid.). Precautions should be taken to keep storage areas clean, dry, and free of any reactive materials or vapors. Where indoor storage is not employed, containers stored outside should be at least shielded from the effects of direct sunlight, snow and rain. Such a procedure would eliminate operating difficulties often encountered with containers exposed to the elements. Like mechanical equipment, success of operation often derives from preventive maintenance.

The liquid chlorine in containers is under pressure due to its vapor pressure, which in turn is a function of temperature. Fusible safety plugs installed in cylinders and ton-containers are designed to melt and relieve container pressure at elevated temperatures. For this reason the containers should be kept cool and away from flammable substances or any conditions that might contribute excessive heat. Storage at about room temperature is a good method to avoid some of the feeding difficulties which will be discussed later and if containers must be stored outside, arrangements should be made to heat the container shelter to room temperature. Chlorine storage buildings should be designed fire resistant. Storage areas should have two exits permitting ready escape for personnel. Personnel should be aware of safety precautions and the use of safety equipment, which should be readily available in a safe location and periodically checked. Information on safety equipment and precautions can be obtained from the Chlorine Institute, Inc.

Ease of container handling is another facet of storage design. Hoisting devices should be able to reach any container without undue difficulty. Cylinders are customarily placed on end. Ton containers are stored on their sides preferrably slightly elevated from the floor to keep them easily accessible and dry. The ton containers are often placed on cradles or I-beams to prevent rolling. The stacking of chlorine containers, whether they be cylinders or ton containers, is poor practice in that a leaking container would be difficult to remove.

Containers should be used in the order they are received. Handling techniques should be designed to accomplish this as well as to avoid containers being struck in transport and in storage. The protective valve covers should be kept on at all times unless the container is in use.

"Stationary storage" of liquid chlorine in large permanent storage tanks is not recommended by the Chlorine Institute (Ibid.) for several reasons:

1. Specialized training and experience for operation and maintenance.
2. Emergency disposal of chlorine.
3. Mobility in case of fire.

Container Service Connection. Chlorine can be extracted from the various containers as either a liquid or a gas. Chlorine is customarily taken from cylinders as gas; by nearly inverting the cylinder and securing it in that position the liquid can be extracted. Ton containers are positioned for service with the two service valves vertical to each other. Gas can be extracted from the upper valve and liquid from the lower one. Railroad tank cars are designed for liquid extraction, but the car dome contains two valves for gas extraction if necessary.

All the details of container service attachment will not be covered here but can be found in The Chlorine Manual, published by the Chlorine Institute, Inc. which presents an excellent coverage on this and related subjects, including safety precautions. This booklet should be an integral part of all sewage plants using chlorine.

The service valves on cylinders and ton containers are identical with the exception that those for ton containers do not incorporate the fusible safety plugs. "Outlet threads on cylinder and ton container valves are not standard pipe threads, but are special straight threads (1.030-14NGO-RH-EXT) which conform to connection #660 of American Standard B57.1," Chlorine Institute (1962b). Connections that do not fit should never be forced. Service valves for railroad tank cars are somewhat larger.

Before the valves can be service connected the containers protective valve hood must be detached followed by the valves outlet cap and gasket. The valve hood is designed to protect the valves from damage and the outlet cap is intended to keep out dirt, oil, and other foreign matter. In railroad tank cars the four valves in the dome are protected by plug fittings. Before the valve caps and gaskets or plugs are removed, the operator should be sure that the valve is completely closed. The line connection to the service valve can be either of the union type or yoke type (also called the clamp and adapter connection), Laubusch (1959b). A valve auxiliary to the container valve will minimize chlorine loss during container changeover and will provide a convenient shutoff if the container service valve should prove to be defective, W&T #5.110.

Common sense dictates that connections should never be forced on container service valves or on any piping containing chlorine, nor should service valves that are tight be opened or closed with unreasonable force. The 3/8 inch square box wrench used to open cylinder and ton container valves should not be over 6 inches in length and that used for railroad tank cars (pipe wrench) should not be over 18 inches long, Laubusch (1959b). To permit maximum discharge, the valves need only be slowly turned one counter-clockwise revolution.

The secured connections to service valves should always be checked for leaks. This is customarily performed by holding a swab dipped in ammonia water near the connection. A chlorine leak will cause formation of a white cloud (ammonium chloride). The ammonia water used for this operation should be of commercial strength (26° Be'*). Household ammonia is too weak, Chlorine Institute (1959b).

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*Be' = degrees on a Beaume hydrometer. For liquids heavier than water Be' = 145(1-1/s) where s is the specific gravity of the liquid. 26° Be' ammonia water is 29.4% NH_3, Fair and Geyer (1959).

Discharge Rates. The physics of chlorine gas discharge from cylinders and other containers is often confusing to the sewage plant operator and others. The action of chlorine being withdrawn from a container of liquid chlorine is analogous to water being heated to produce steam, however, the temperature required for the boiling of water (100°C) is considerably higher than that for chlorine (-34.05°C). The rate of vaporization and vapor pressure, whether it be for water or chlorine, is dependent only on temperature. Thus, connection of two or more containers at different levels of fullness is feasible and this will aid in prevention of running out when the plant is unattended.

Each container will discharge at the same rate if their temperatures are the same, VanKleeck (1956). At low discharge rates with sufficient atmospheric heat available (123.7 BTU/lb. at the chlorine boiling point) the vaporization rate and pressure will remain fairly constant and a constant flow rate maintained, Chlorine Institute (1959b). The chlorine liquid in the container will fall below room temperature and so it is important for reliable chlorine discharge to maintain the chlorine room at a moderate, constant temperature preferrably between 70° and 80°F. To obtain slightly higher extraction rates of chlorine gas, the room temperatures can be increased and air circulation about chlorine containers improved by using a fan. The application of direct or excessive heat should be avoided. If a manifold is available more cylinders and ton containers could be connected. Excessively high discharge from a container will result in the formation of sweat or even frost on the container which in turn will impair heat transfer.

The maximum dependable extraction rates at room temperature are stated in the literature as being about 30-40 pounds per day for 150# cylinders and 400-450 pounds per day for ton containers. These rates can be doubled for short periods but will produce some sweating and frosting, Laubusch (1963). Maximum rates under normal conditions are a function of container temperatures and the container employed as indicated below, WPCF (1961).

TABLE 4

Temperature °F	Maximum Discharge in Pounds Per Day		
	105# Cylinder	150# Cylinder	Ton Cylinder
40	6	9	100
50	14	21	240
60	23.7	35.5	385
70	32	47.5	536
80	41.2	62	700

If higher feed rates are necessary, the above Table infers the employment of a larger container. However, if gaseous extraction is insufficient or inpractical, liquid chlorine then could be extracted. At 70°F against a 35 psi pressure, liquid chlorine can be extracted from cylinders at a rate of 200 pounds per hour and from ton containers at 400 pounds per hour. Tank cars, which are designed to discharge the liquid, can emit up to 8000 pounds per hour from each valve. Safety devices will not permit more. The internal pressure of tank cars under normal conditions is sufficient to provide adequate discharge, however, where the air temperature may be low or where the liquid must be discharged to a high elevation, the tank car can be pressurized (padded) with the introduction of oil-free, dried, clean compressed air as recommended by the Chlorine Institute. In some cases the tank cars can be ordered "pre-padded." Since chlorine is not introduced to sewage as a liquid, it must first be transferred to the gaseous state which is the function of the "evaporator."

Inventories, Joint Committee (1953). "Critical inventory of chlorine at a water or sewage treatment plant is defined as the number of unconnected (full) chlorine units equal to the number of units normally connected and in service. Except for systems using less than 5 lbs. per day or for unusual circumstances, this type of inventory should not be condoned. A plant should be considered in emergency operation with this limited inventory."

"Working inventory of chlorine at a user's plant may be defined as that inventory which represents a reasonably ample supply to assure continuity of the disinfection treatment. In practice it should approximate a) a duplication of the connected chlorine units (critical inventory), b) a chlorine reserve equivalent to the length of time required for delivery from the shipping point to the user's plant (varies from 2 to 15 days' supply of chlorine, depending on local conditions), plus a chlorine reserve for emergencies, etc. equivalent to a 15-day supply. The working inventory for any plant must be developed specifically for that plant and be based on actual conditions."

"Maximum inventory is defined as that inventory which is equivalent to a 60-day supply of chlorine at the user's plant at normal rates of use. The small users of chlorine (5 lbs. per day or less) must be excepted from this definition. Beyond the small plant there are few if any practical reasons to exceed the 60-day inventory. To do so ties up an unwarranted stock of containers. Maximum inventories should be considered as being temporary only.

Tables 5 and 6 have been prepared to summarize these.

Hypochlorites Management

Reason for Selection. The decision whether to employ gaseous chlorine or hypochlorites in sewage treatment appears in general to be a choice between economics and safety. Hypochlorites are relatively expensive and consequently are economically feasible only at small sewage plants where the amounts required are small or where a local industry has it available as a by-product that can be obtained at lower cost. The equipment required for hypochlorite application is fairly simple and generally of low initial cost, AWWA (1951). Regardless of their cost, the application of hypochlorites is often necessitated by circumstances such as in areas of high population density (where liquid chlorine leakage could be disastrous) or as required by local or state regulation.

Hypochlorites occasionally are employed in larger water and sewage plants as a standby disinfectant, however, the choice of using liquid chlorine or chlorine compounds, as stated by Laubusch (1960b) is primarily a consideration of plant size, volume, water character, treatment objectives, continuity of operation, safety considerations, availability and comparative costs of materials, facilities and personnel required for handling, storage, maintenance, effects on other processes, state or local requirements.

All the hypochlorites deteriorate to some degree depending upon the particular compound, thus necessitating periodic quality testing and feeder adjustment. Just as liquid chlorine impurities can clog

TABLE 5 RECOMMENDED CHLORINE INVENTORIES AT WATER AND SEWAGE PLANTS (1)

Joint Committee on Water Supplies (1953)

Ave. Cl_2 used #/day	Critical Inventory (2)(3)	Working Inventory(2)	Maximum Inventory(2)
0.5	1 150# cylinder	1 150# cylinder	2 150# cylinder
2	1 150# cylinder	1 150# cylinder	2 150# cylinder
5	1 150# cylinder	1 150# cylinder	3 150# cylinder
10	1 150# cylinder	3 150# cylinder	4 150# cylinder(4)
20	1 150# cylinder	4-5 150# cylinder(5)	8 150# cylinder(4)
50	2-3 150# cylinder	8-12 150# cylinder(5)	20 150# cylinder(4)
100	3-5 150# cylinder	16-24 150# cylinder(5)	40 150# cylinder(4)
200	6-8 150# cylinder	30-47 150# cylinder(5)	80 150# cylinder(4)
300	1 ton container	4-6 ton container(5)	9 ton container(4)(6)
500	2 ton container	8-10 ton container(5)	15 ton container(4)(6)
1000	2-4 ton container	12-18 ton container(5)	30 ton container(4)
2000(7)	4-6 ton container	22-35 ton container(5)	60 ton container(4)

(1) 100# cylinders are available. Where they are used instead of the 150# cylinders, the net weight of chlorine in inventory should substantially agree with that shown.

(2) None of which is in use.

(3) Also represents the number of cylinders or containers usually in service. Local conditions could affect these figures materially. Inspection of the number of units in service the principle as expressed in the definition of critical inventory should still apply.

(4) Roughly represent 60 days of chlorine inventory.

(5) The smaller number represents the working inventory where deliveries require 2 days; the larger represents the working inventory where deliveries take 15 days.

(6) Maximum inventories listed for these categories are for plants receiving chlorine delivery by truck. For plants receiving chlorine delivery by railroad car (15 1-ton containers) the maximum inventories should be 19 and 23 ton containers, respectively, for plants using 300-500#/day.

(7) Users of 1 ton or more of chlorine per day should consider the use of single-unit tank cars.

TABLE 6 RECOMMENDED MINIMUM CHLORINE INVENTORY(a)

Max. Chlorine Use #/day	Inventory of Chlorine Containers			Approx. Total Supply-Days
	In Service	In Reserve	In Storage or in Transit	
10	2 150# cylinder	2 150# cylinder	-	60
40	2 150# cylinder	4 150# cylinder	4 150# cylinder	37
100	4 150# cylinder	4 150# cylinder	10-15 150# cylinder	27-34
200	6 150# cylinder	6-10 150# cylinder	20-30 150# cylinder	24-34
	or			
	1-2 2 ton container	1 ton container	1 ton container	30-40
400	10 150# cylinder	10-20 150# cylinder	50-60 150# cylinder	26-34
	or			
	1-2 ton container	1 ton container	3 ton container	25-30
1,000	4 ton container	2 ton container	7-9 ton container	26-30
1,500	4 ton container	4 ton container	10-15 ton container	24-30
2,000	6 ton container	4 ton container	10 ton container & 1 TMU car	35
	or			
	2 ton container with evaporator	4 ton container	14 ton container & 1 TMU car	35
3,000(b)	2 ton container	6 ton container	15 ton container & 1 TMU car	25
	or			
	1 tank car(30T)	-	1 tank car(30T)	40
4,000(b)	4 ton container	8 ton container	15 ton container & 1 TMU car	21
	or			
	1 tank car(30T)	-	1 tank car(30T)	30
5,000(b)	4 ton container	8 ton container	15 ton container & 2 TMU cars	22
	or			
	1 tank car(30T)	-	1 tank car(30T)	24
10,000(b)	6 ton container	8 ton container	25 ton container & 3 TMU cars	17
	1 tank car(30T)	-	2 tank car(30T)	18
	1 tank car(55T)	-	1 tank car(55T)	22

(a) From Wallace & Tiernan, Inc., Cat. Sheet No. 5.070

(b) With evaporator.

Note: In general, increase number of 150# cylinders shown by one-third when using 100# cylinders.

chlorination devices, so too can some hypochlorite sludges clog feeding equipment. The more trouble-free and expensive sodium hypochlorite is the predominant disinfectant for private swimming pools and appears to be gaining some popularity in sewage treatment.

Storage and Handling. As was true in the case for liquid chlorine, principles and recommendations for hypochlorite storage are based upon a few simple characteristics of the compounds. For example, all of the hypochlorites are weakened in their oxidizing ability by heat and moisture. Thus it is always recommended to store this compound in a cool, dry area. These compounds also have the characteristics of being oxidizers, highly corrosive, and will emit chlorine-like odors. Thus containers should be kept clean, constructed of relatively inert materials, tightly covered but not airtight, and, when possible, segregated from other chemicals. Leaking containers, of course, should be immediately removed from storage.

Of the chlorine compounds used in sewage treatment, the high-test hypochlorites are the most stable, but are not absolutely so as pointed out by Laubusch (1960a):

> "Although product deterioration commences with packaging operations, storage at 86°F for one year reportedly reduces the original available chlorine content (weight) by only about 10 per cent. Cooler storage temperature reduces the deterioration to a smaller amount."

It is good procedure to purchase the chlorine compounds in such amounts as to provide reasonable turnover and to avoid excessive storage and deterioration.

The chlorine compounds are reactive enough with certain compounds to cause a fire or explosion. The American Water Works Association recommends avoiding their contact with organics, hot sulfur jointing compounds, activated carbon, and finely divided metals, AWWA (1951). Laubusch (1960a) also recommends avoiding contact with turpentine, ether, oils, sugar, fats, and oxidizable materials.

Besides the usual disadvantages of chlorine compounds, sodium hypochlorite is also light sensitive, and thus, it is recommended to store this compound in dry, cool, dark areas, or at least in containers protected from light. One manufacturer's NaOCl product, as given by Laubusch (1960a), has the following deterioration rate:

TABLE 7

Trade Available Chlorine %	Half Life in Days at 77°F
3	1700
6	700
9	250
12	180
15	100
18	60

Most manufacturers recommend a maximum shelf life of from 60 to 90 days (Ibid.). Sodium hypochlorite is strongly alkaline or caustic and care should be taken in handling. Use of protective clothing and gloves is good practice.

Chlorinated lime rapidly deteriorates and will absorb moisture at high rates when exposed. To gain the best effects when using this compound, storage in cool, dark, dry areas is imperative and compound strength should be checked routinely.

Transport. Shipment is governed by regulations of the Interstate Commerce Commission Recommendations for containers and their care in storage apply to shipment as well.

The types and capacities of shipping containers are as follows, AWWA (1953):

Compound -- Chlorinated Lime; Calcium Hypochlorite; Sodium Hypochlorite Solution.

Containers -- 100 or 300 lb. sheet-iron drums; 5 lb. cans up to 100 lb. metal drums; 2.5 to 13 gal. glass carboys or plastic containers; 50 gal. rubber lined drums or tank truck for large deliveries.

Containers must be labeled correctly for shipment as to poison, antidote, corrosive nature and flammabilities.

DESIGN OF FACILITIES

In-Plant Transport

Chlorine applied from railroad tank cars, truck tanks, and permanent storage facilities can be considered as stored at point of application. Chlorine cylinders and ton containers, however, must be brought from a storage area and connected to the chlorination system. Cylinders customarily do not require a hoisting device and are usually transported in the plant manually. Sewage plants employing ton containers do need hoisting devices and about half the plants in this country presently use electrical hoists, ASCE (1963). When ton container changeover is frequent, it is good practice to use powered travelling hoists. The hoist should have a minimum capacity of 2 tons and it should be equipped with an approved type of lifting-beam container grab (Ibid.).

When designing container hoists, consideration should be given to wide mobility and sufficient headroom. If greater chlorine usage is required, the chlorine room arrangement should be designed to accept additional containers if necessary and to have the means to transport these containers to the areas reserved for expansion. The problem of insufficient headroom was observed at a sewage treatment plant (in Rhode Island) in which the hoisting facility could not lift emptied ton containers over other containers still in service. Consequently, in order to change the empty container, the one in use had to be removed, thereby shutting down the entire chlorination system. Such a situation could possibly be rectified by use of (1) a shorter hoist, (2) standby chlorination, (3) emergency chlorination during container changeover, or (4) rearrangement of containers in the room. The situation cited was corrected by means of the latter plan.

The Chlorine Room

The ASCE-Manual of Engineering Practice-No. 36 entitled "Sewage Treatment Plant Design" enumerates several recommendations regarding the housing of the chlorination system as paraphrased below:

Safety.

1) The chlorine rooms should be isolated from the rest of the control building.
2) A means of observing the chlorine equipment without entering the room should be provided.
3) It is good practice to separate the chlorinator room from the chlorine container room or storage area.
4) Access to the chlorine rooms, equipped with panic hardware, should be made through an exterior door opening outward.
5) Where access to the chlorine rooms must be made through interior doors opening inward, they should be equipped with doors closers and gas-tight weather stripping.
6) The vent fan control and emergency gas mask should be located outside the chlorine rooms.

Space.

1) Sixty-four square feet is adequate for small sewage plants with a single chlorinator and a chlorine dosage rate of less than 200 pounds per day.
2) Plants using two chlorinators with a total feed rate of up to 400 poundsper day should have a minimum of 100 square feet.
3) Where ton containers are used with evaporators, 160 square feet is needed for each chlorinator-evaporator unit plus 100 square feet for each ton container.
4) Containers handled by hand require a ceiling height of at least 8 feet 6 inches.
5) Containers handled by mechanical means require a ceiling height of not less than 11 feet 6 inches.

Ventilation.

1) Ventilation is required for all chlorine equipment rooms.

2) Ventilation intake or exhaust fan should be located at the floor level.

3) Best technique is to use an exterior exhaust fan with air intake duct running to the chlorine room floor.

4) The fresh air intake should be through a louvered entrance door or a separate air intake.

5) Good practice calls for an exhaust system that will give a complete air change every 3 minutes.

Heating.

1) A minimum temperature of 70°F should be maintained.

2) A hot water heating system is preferred for safety considerations and uniformity of temperature.

3) Forced hot air is not recommended unless confined only to the chlorine rooms.

Scales and Depletion Alarms

Chlorine containers are placed on to scales in the chlorine room when in service. The scales provide the plant operator a means of determining the amount of chlorine that remains in the container, and, therefore, the amount that has been applied. Chlorine gas pressure in the chlorination system is a poor indicator of container content considering that chlorine vapor pressure is theoretically a function only of temperature and not of mass in the container, Laubusch (1959b).

Scale capacity as recommended by the ASCE (1963) should be sized to accommodate conditions at the maximum chlorine feed rate. Commercial scales are sold generally in capacities ranging from 1,000 pounds up to 10,000 pounds, which will receive anywhere from three up to twenty-four 150-pound cylinders or from a single ton container to 5-ton containers (Ibid.).

The scale platform arrangement is often dictated by the type of chlorine container employed. For example, if cylinders are used, the scale platform should be level with the floor to avoid lifting of the cylinders. The floor recession required for this arrangement must be equipped with a drain. A scale built within a pit or floor recession or one constructed in a steel box bolted to the floor is termed a "dormant scale." A "portable scale," or one of small capacity if fitted with wheels, is at times employed, however, the wheels are usually removed for use in water or sewage plants, W&T #5000.

Figure 1 shows typical scale and container arrangement.

Ton containers are customarily placed on scale platform arrangements located up off the floor for better ventilation and easier access to the container valves. The scale platform device for ton containers can be bolted to the floor instead of recessed unless there is a likelihood of scale damage during container changeover as might be the case if a lift truck and skids were used to transfer containers. Ton containers, however, are usually conveyed by a hand or electric operated hoist which neatly lifts or sets down containers directly over the scales. Crane scales, resembling a crane hook with an attached dial, can be purchased with high capacities and could be used as standby scales.

"Track scales" are used in conjunction with railroad tank cars. The railroad siding tracks upon which the tank car rests is a part of the scale mechanism built within a pit below the tracks. The indicating device is located above ground along side the tracks and can be of two types -- beam or dial. The beam scale indicates the weight by the use of a mass slid along a numbered beam until balance is achieved. Counterpoise masses can be used to extend the capacity of the scales. Dial

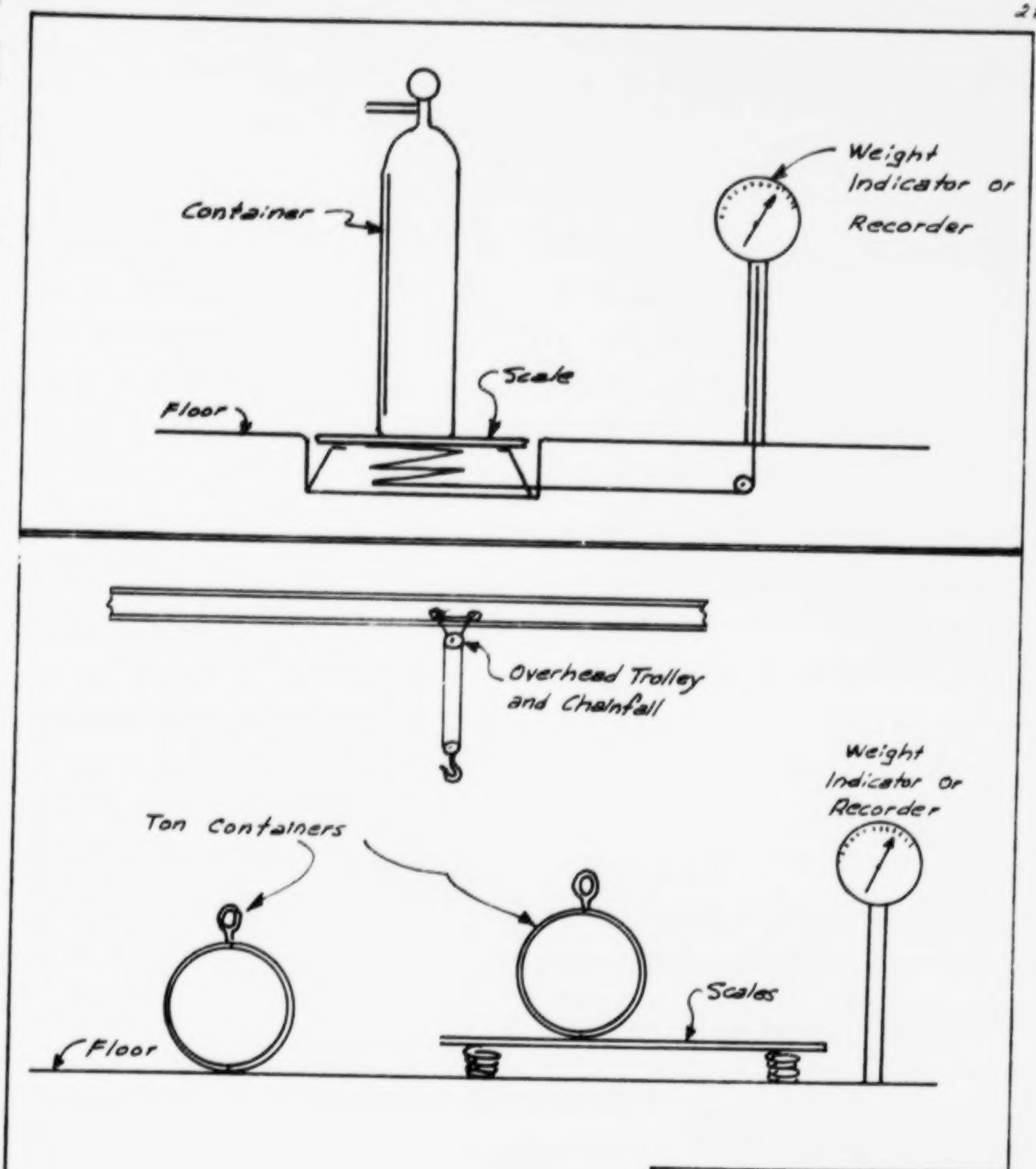
Container
Weight Indicator or Recorder
Scale
Floor
Overhead Trolley and Chainfall
Weight Indicator or Recorder
Ton Containers
Scales
Floor

FIGURE 1

TYPICAL
SCALE SETUPS

NEMHSL, FRD, SQZ MAY, 1967

scales indicate the weight directly by an indicator and a graduated plate. Dial scales which indicate the net weight of the container on the dial while the total weight is carried on two beam scales integrated in the device are available. Where desired, a loss of weight recording device can also be incorporated in this scale (Ibid.). The dial type scale is desirable because it permits easy determination of the amount of chlorine remaining at any time, which is simply the gross weight of the container minus the container weight when empty (the specified weight is stamped on the container side). Since it is good practice for sewage plant operators to check the chlorine scales frequently, use of the dial-type scale will make this task easier.

One situation too often encountered at some sewage plants is depletion of the chlorine containers without awareness of the plant operator which results in a decrease or even a complete shutdown of the plant's chlorination. Rather than relying upon the alertness or memory of the operator, at least in those plants where chlorination is critical there should be a warning system of container depletion. Where operators are not on duty full time throughout the day, the warning systems should be transmitted to those parties (for example, the police or fire department) able to eliminate the situation or quickly contact someone who can. Such devices are commercially available.

"Any dial scale may be equipped with a magnetic mercoid switch and relay, set to make contact when the weight of chlorine on the scales reaches a predetermined and adjusted minimum. When the contact is made, an alarm system may be energized " (Ibid.).

Beam scales can be similarly installed with a loss-of-weight recorder and alarm system.

Alarm systems are also available for other situations. Wallace and Tiernan #50.100, for example, advertises:

> "-Over and under deviations from set feed limits on Merchen Scale Feeders.
>
> -High and low temperature thermostats on liquid chlorine evaporator.
>
> -Low pressure switches on the water supply.
>
> -High and low pressure switches on the chlorine supply.
>
> -Chlorinator vacuum switches indicating injector clogging, failure of the injector water supply, or other operating difficulty.
>
> -Alarm switch is the Wallace and Tiernan Type A-485 Chlorine Flow Recorder indicating exhausted chlorine supply or failure of the injector water supply.
>
> -Limit switches in the Wallace and Tiernan Residual Chlorine Recorder indicating residuals outside preset limits."

Standby

During chlorine container changeover, chlorine should still be applied to the sewage. This can be accomplished with a standby container attached to the system and discharging chlorine during the period that the depleted containers are replaced. There are a number of systems or techniques that could be employed. The standby container, for example, could be housed on separate scales, or else fresh containers could be attached to the system prior to each changeover and removed to storage afterwards, or the sewage flow could be halted if nothing else is possible. In the case of railroad tank cars, consideration should be given to twin sidings and the related appurtenances to insure uninterrupted chlorination. Regardless of what changeover chlorination technique is employed, it should have the character of being quickly and effectively employed.

Piping and Manifolds

Dry. "Dry" chlorine refers to the chlorine extracted from the container as yet unmixed with water. Chlorine as such is relatively inert as compared to the highly corrosive character of "wet" chlorine, meaning mixed with water or hydrolyzed. Recommendations for piping and pipe layout for dry chlorine take into account the pressure involved with vaporization of contained liquid chlorine, the retention of chlorine through conduits in a single phase (either as a liquid or gas), and the prevention of chemical reaction with certain compounds. Usually, chlorine piping from cylinders is designed for gaseous extraction and that from ton-containers, railroad tank cars, and storage facilities are designed for liquid conduction.

Specifications and recommendations of materials and appurtenances are rather voluminous and will only be touched upon. Those interested in specifics on this subject can refer again to the Chlorine Manual. Figure 2 presents a schematic diagram of chlorine piping.

Dry chlorine is not corrosive to most common metals below 300°F except aluminum, Laubusch (1959b). Short lengths of copper tubing are used as connection lines from chlorine containers. This facilitates connection to the containers as well as providing some allowance for vertical movement of the scales as the containers are discharging. The copper tubing should be annealed and able to stand pressure up to 500 psig (3/8" O.D. x 0.035" wall), Chlorine Institute (1959b). Since tin is also attacked by dry chlorine, jointing materials used on soldered joints must be of pure lead, AWWA (1951). The flexible copper tubing is connected from

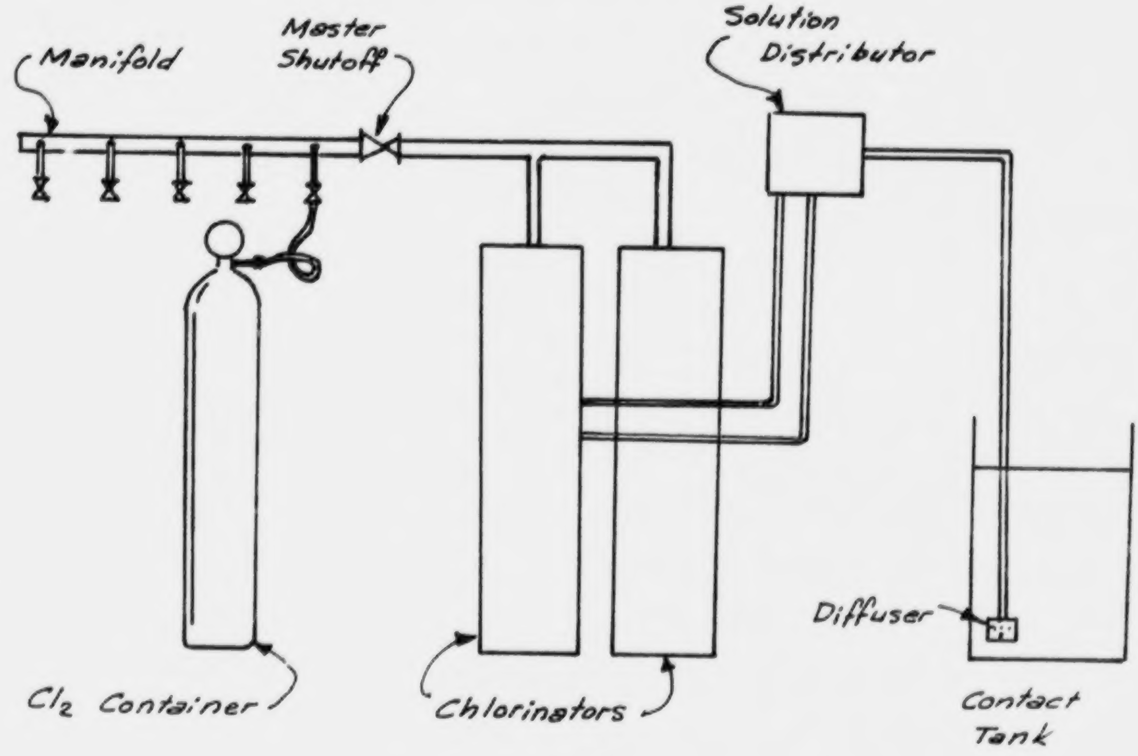
Manifold
Master Shutoff
Solution Distributor
Cl2 Container
Chlorinators
Diffuser
Contact Tank

FIGURE 2

SCHEMATIC OF TYPICAL CHLORINATION PIPING

NEMHSL, FRD, SAJ MAY, 1967

the container to stationary piping leading to the chlorinator or evaporator. The stationary piping must also be of a heavy duty (250 psi), black steel, wrought-iron, or copper with at least a 3/4 inch diameter (Ibid.). Commonly 3/4 inch and 1 inch diameter pipes are employed with threaded joints, Wallace & Tiernan #5.110. Pipes from 3/4 inch up to 1-1/2 inch diameter can also be butt welded, flanged, or socket welded at their joints. Pipes with over 2 inch diameters are either butt welded or flanged, Laubusch (1963).

Spring loaded or gravity-operated check valves are not recommended (Ibid.). Appurtenances likewise should be of acceptable materials and of proper strength.

Piping layout recommendations for chlorine gas and liquid are similar with a few exceptions. All chlorine piping systems are recommended to be as unobstructed as feasibly possible. This means an avoidance of unnecessary fittings, traps, loops, valves, and like obstructions. This recommendation is intended to avoid a retention of chlorine in the piping system when a section is shutoff for maintenance or other purposes. The piping system should be well supported, not be subject to extremely high or low temperatures, be designed for expansion allowance, and be clear of and protected from activities liable to result in damage to the piping.

Gaseous chlorine under certain circumstances can condense in the piping system and choke the flow. Low temperatures in the piping could cause this situation and for this reason it is recommended that the piping be kept 5-10°F warmer than the container, Wallace & Tiernan #5.100.

To accomplish this it is often times sufficient to run the piping high up in the chlorine room where the air is usually warmest. If this is insufficient, insulation could be applied to the piping or even a pressure reducing valve attached near the container will prevent condensation in the piping system. This latter recourse is especially applicable to situations where there is a drastic daily change in temperature (Ibid.). The piping should be inclined upward from the container. Low points should be equipped with "drip legs" to catch reliquified gas. If condensation trapped within the drip leg is not evaporated, the apparatus could be warmed by a 100 watt light bulb, AWWA (1951).

Conduction of liquid chlorine should be designed to prevent vaporization of the liquid, which could develop a high hydrostatic pressure even to the point of bursting the piping. The specifications for gaseous chlorine piping also applies to that for liquid chlorine. Liquid chlorine lines should be kept cooler than the container so it is best to run them through low, cool areas to avoid any vaporization of the liquid. These lines should be as short as possible. Situations where the liquid might be retained in the piping, for example, between two shutoff valves, should be avoided if at all possible; but if this situation exists, a properly designed expansion chamber (empty 100# or 150# chlorine cylinder inverted, secured, and connected to the line by a tee connection) should be employed, Wallace & Tiernan #5.100. Trapping of liquid chlorine occurs often times, though only momentarily, between the container and a chlorine-evaporator during changeover. Good practice dictates that under these circumstances the valve at the container be

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Wet. The solution of chlorine gas and water (solution water) is highly corrosive and materials in contact with it should be corrosion resistant as well as strong if the solution water is under pressure.

Piping for direct feed chlorination is usually of small diameter silver tubing (less than 1/4 inch diameter) and is recommended to be as short in length as possible (less than 25 feet), Wallace & Tiernan #5.200.

Piping for solution feed chlorination is somewhat more varied and selection should consider material strength, corrosion resistance both inside and outside, and friction head loss. The solution water presure will affect the choice of material and the conduit design. At low (0-5 psi) pressures, for example, conduits made of chemical stoneware, concrete, glass, porcelain, certain alloys, hard rubber, PVC, Haveg, glass-fiber reinforced Hetron resin, Kel-F, Saran, or Teflon will suffice (Chlorine Institute (1959b)) if properly designed to handle the solution pressures be they positive or negative. At higher pressures metals resistant to corrosion by chlorine water may be used such as gold, platinum, silver, or titanium. However, rubber or plastic lined metal pipes are more commonly used (Ibid.). High pressures are not generally found in sewage treatment. Unless friction loss is desirable, under a situation where there might be a considerable drop in elevation of the solution water from the injector to the point of application, the solution water lines are kept ordinarily as short as possible to keep the friction head loss less than 5 pounds per square inch.

Rubber-lined steel pipe is used in larger sewage plants for solution water conduits starting at a diameter of 1-1/2 inch on up. The rubber employed is made resistant to chlorine corrosion and diffusion, temperature changes and aging. It is specified for example by one manufacturer to be 1/8 inch thick in pipes up to a 5 inch diameter and 3/16 inch for 6 inch diameter pipe and up. The metal is of standard black seamless steel and is available up to lengths of 20 feet, Wallace & Tiernan #5.240. All fittings and pipe ends are of the flange type. The pipe should be specified to be properly prepared for rubber coating, be of adequate tolerances, that pipe exteriors are properly finished, that the rubber coating be of acceptable quality, that all flanges be secured, and that the finished product be tested for leakage in the lining, op cit.

For less demanding projects rubber hose up to 2 inch diameter can be employed, ASCE (1963). The hose can be of wrapped rubber (up to 2 inch diameter) or molded hoses (up to 1-1/2 inch diameter) which are available in longer lengths, Wallace & Tiernan #5.250. Where a rubber hose is used a metal trough or conduit might be employed as a support and protection to the hose. The hose can be internally supported for negative pressures that might occur.

Plastic pipe and plastic lined metal pipe can be used and are found to be resistant to the reactivity of chlorine dioxide (Ibid.). The rigid plastic used may be Kralastic, and high impact polyvinyl chloride (PVC). Plastic pipe has the advantage of being threaded or chemically welded in sizes up to a 6 inch diameter with ordinary technique and tools. Plastic piping does, however, require more supporting or bearing than required for the metal pipes (Ibid.). Flexible polyethylene plastic pipe, up to a 3 inch diameter, can be obtained up to a 400 foot length, which is compatable to situations requiring a flexible corrosive resistant (inside and outside) or long conduit. Similar to the rubber hose, the plastic pipes may be connected by couplings and clamps.

Where visibility or complete corrosion-resistance is desired Pyrex glass pipes with flanged joints are available in diameters from 1 inch up to 6 inch in lengths up to 10 feet (Ibid.).

Manifolds. In situations where more than one cylinder or container must be used to meet the chlorine requirement, a manifold is usually provided to permit simultaneous chlorine discharge to the chlorinator. Manifolds are recommended to be used only with gaseous chlorine, Laubusch (1963). They can be designed to receive any number of service connections from cylinders and ton containers. Its strength and material should conform to that required for standard piping of chlorine. Control can be obtained by the shutoff valves on the container ends of the service connections and a master shutoff valve at the manifold discharge. However, the designer should be cognizant of the head loss through such devices and the conditions necesssry to obtain sufficient chlorine gas pressure at all times. A sketch of a manifold system is included in Figure 2 of piping.

As long as each container discharging to a manifold system is at the same temperature, each container will have the same vapor pressure and will discharge at the same rate and the system will be in equilibrium. If for example a cold container (perhaps one stored outside under winter conditions) is added to the manifold system, the equilibrium will be disrupted. The vapor pressure in the cold container will be less than that of the warmer containers which might be visualized on examination of Figure 3. There will initially be a push of gas into the cold cylinder and condensation of the gas there possibly such as to completely fill the cold container with liquid chlorine. As the cold container warms, the liquid inside will vaporize, and this container too will reach equilibrium with the others. This process, of course, will be reversed if a warm container is attached to a manifold system with cooler containers. These situations present no real problems unless a cool container entirely filled with condensed liquid chlorine should by some reason have its service valved closed. As this container becomes warmer the vapor pressure increases and the liquid density (Table 8) decreases such as to increase the possibility of the container bursting. The best policy is never to close off service valves of containers under such circumstances and to keep the in-service and reserve containers in the same ambient temperatures. Extreme temperatures, of course, should be avoided. Employment of a twin set of containers, scales, and manifolds used alternately would avoid this problem.

Chlorine Contact Tanks and Mixing

One of the fundamentals of chemistry states that in order to achieve a proper reaction or solution of two substances, they first must be thoroughly mixed. Contrary to what may be practiced at many sewage plants, chlorination is more than just a mere "formality." It is perhaps the most important step in the treatment process. The success of it depends upon the completion of innumerable sophisticated chemical reactions. With little regard given to proper mixing of sewage and chlorine part of

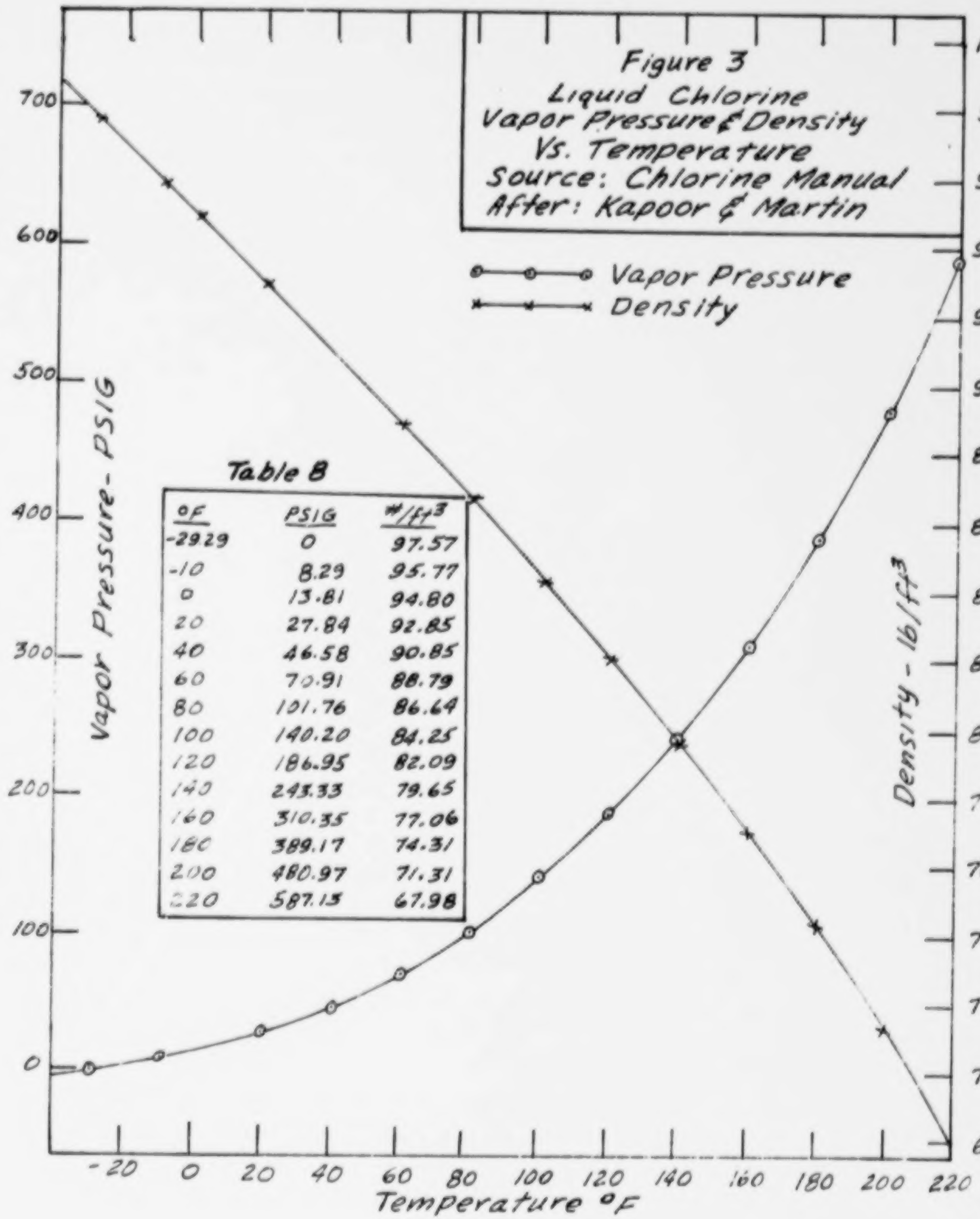

Figure 3
Liquid Chlorine
Vapor Pressure & Density
Vs. Temperature
Source: Chlorine Manual
After: Kapoor & Martin

Table 8

°F	PSIG	#/ft^3
-29.29	0	97.57
-10	8.29	95.77
0	13.81	94.80
20	27.84	92.85
40	46.58	90.85
60	70.91	88.79
80	101.76	86.64
100	140.20	84.25
120	186.95	82.09
140	243.33	79.65
160	310.35	77.06
180	389.17	74.31
200	480.97	71.31
220	587.15	67.98

the sewage may be adequately chlorinated and the rest essentially unaffected, a wasteful use of chlorine and unsatisfactory disinfection. Since some chlorine contact chambers are designed like sedimentation tanks to retain sewage with little induced turbulence, they can hardly be expected to provide the necessary mixing.

Heukelekian and Day (1951) studied 4 chlorine contact chambers for mixing of chlorine solution and sewage. Using the amperometric titration in their chlorine residual measurements they found that with inadequate mixing of the chlorine solution with sewage most of the chlorine passed along the contact tank bottom with the surface sewage being underchlorinated. There was too little turbulence in the chamber to induce adequate mixing within the contact period. Under these conditions, there would be a variation of bacteria concentration and chlorine residual with the depth, a situation whereby one could indicate anywhere from excellent to poor results of chlorination depending upon what depth in the chamber the sample was taken.

Eliassen (1948) indicated that some kind of mixing was necessary between chlorine solution water and sewage. Though initial mixing induced no significant change in coliform group MPN values of an unchlorinated sewage, he proved statistically that lower MPN values were obtained by initial mechanical mixing of the chlorinated sewage. He also found no statistical difference between rapid and slow mixing.

Heukelekian and Day (1951) indicated that when chlorine was added to sewage without a mixing chamber, there was poor chlorine distribution with around-the-end type baffling but found excellent distribution of the chlorine using a mixing chamber. With hydraulic-induced turbulence or mixing, there was no need for mechanical mixing. Vertical channels or relatively shallow mixing compartments ahead of the chlorine contact chamber designed to induce turbulence provided adequate chlorine distribution. Over-and-under baffling, 2 to 3 feet from the channel bottom provided adequate mixing.

The chlorine contact tank is one of the most important facets of good chlorination practice, yet there appears to be little mention of proper contact tank design in the literature. The shape of this device may be rectangular, circular, or simply the plant effluent pipe, ASCE (1963).

Due to tendency of the chlorine contact tank to act as a sedimentation tank the designer may under some circumstances provide scum and sediment removal devices in the tank, Keefer (1940). Provisions should be made to clear or flush out the contact tank periodically, especially subsequent to primary treatment, where detention times may be designed to be longer, VanKleeck (1956b).

Detention periods may be designed for a minimum actual contact interval of 15 minutes prior to discharge (ASCE, 1963) or commonly from 15 to 30 minutes based upon average maximum sewage flow, VanKleeck (1956b). Detention, however, based upon volume displacement (volume of tank/sewage flow) can be very deceptive, since it is quite possible to have short circuiting through the tank (high velocities fron inlet to outlet, outside of which velocities are low). Detention should be determined by dyes or a salt which would indicate the degree of short circuiting. To avoid excessive short circuiting over-and-under or around-the-end baffling could be placed in the chlorine contact tank, the former having the advantage of providing better mixing of the chlorinated sewage and the latter system being easier to clean. Unless the baffles are positioned correctly short-circuiting will remain a problem. Good mixing of chlorine and influent at the entrance to the contact chamber is most important.

The chlorine contact tanks studied by NEMHSL have shown in dye studies that a portion of the dye moves through the tank rapidly, even under low flow conditions. Estimates of actual detention times using dye indicate that they are less than the design times and can be but 1/3 to 1/2 of the design time. In one instance it was observed that in one tank a section remained uncolored by the dye until almost all of the dye had flowed through the tank. The importance of contact time in disinfection is well established and therefore the design and operation of the contact tank must be scrutinized.

CHLORINE FEED EQUIPMENT

Liquid Chlorine

Evaporation. Where the maximum chlorine use at a sewage plant exceeds 1,000 pounds per day, it is recommended that the chlorine be extracted from the containers in liquid form and converted into gas using an evaporator, ASCE (1963). An alternative is gaseous extraction from a sufficient number of containers attached to a manifold system. It is not considered good practice to discharge the liquid to a manifold system. Customarily only ton containers and tank cars are used to discharge the liquid. Maximum discharge from any container (tank car) is 8,000 pounds per hour, per valve or that allowed by the safety valves of the tank car. The demands for a particular sewage plant should be enough to meet the demands under the worst conditions expected and it is recommended by the ASCE (Ibid.) to employ an evaporator for each chlorinator with a minimum of two, each able to meet the maximum demand.

Evaporators are simply heat exchangers designed to safely convert liquid chlorine to the gas. Liquid chlorine under the pressure of the container is piped to a sealed chamber enveloped by a hot water bath in the evaporator. The evaporating chlorine exerts a vapor pressure to equalize the incoming container pressure and thus determines the liquid level of chlorine in the chamber. The rate of gas use governs the changes of liquid level in the chamber. An increased flow of gas decreases the chamber pressure causing the liquid to rise and increase the volume of chlorine that can be heated to meet the increased demand. At the same time the lower pressure allows more rapid evaporation of the liquid chlorine. Once the chamber and incoming container pressures are again equalized the liquid level will stabilize as well as the flow rate. The water bath temperature is kept fairly constant with thermostatic control devices at around 160°F. Several techniques are commercially employed to heat the water bath such as electrical immersion heaters, steam heat, or piped hot water. Safety features are usually designed within the commercial evaporators and additional devices can be ordered such as high temperature and pressure alarms, Wallace and Tiernan #50.206.

The present day evaporator is a simple device reported to give fairly trouble-free service. Nevertheless, like all machines it occasionally requires some servicing and maintenance most commonly associated with corrosion and scale formation. Some manufacturers attempt to reduce corrosion by cathodic protection of the pressure chamber, Laubusch (1959c). The best protection is a strict schedule of inspection and repair for not only the evaporators but the entire chlorination system. As an added precaution against reliquifaction of the vaporized chlorine, it is recommended that the evaporator be situated in a warm room separate from the chlorine container room, preferably in the one containing the chlorinator. A sketch depicting evaporator operation is presented in Figure 4.

The topic of chlorinators or chlorine feeders will be confined to what is considered to be the main or essential points for background. With the changes taking place in equipment an inquiry to the manufacturers is best for information on the latest developments in chlorinators.

Direct Feed Chlorinators. The direct application of liquid chlorine does not appear to be feasible considering that the boiling point of the liquid under one atmosphere pressure is -29.29°F (-34.05°C), and that solid chlorine hydrate (Cl_2-$8H_2O$) forms below 49.3°F, Chlorine Institute

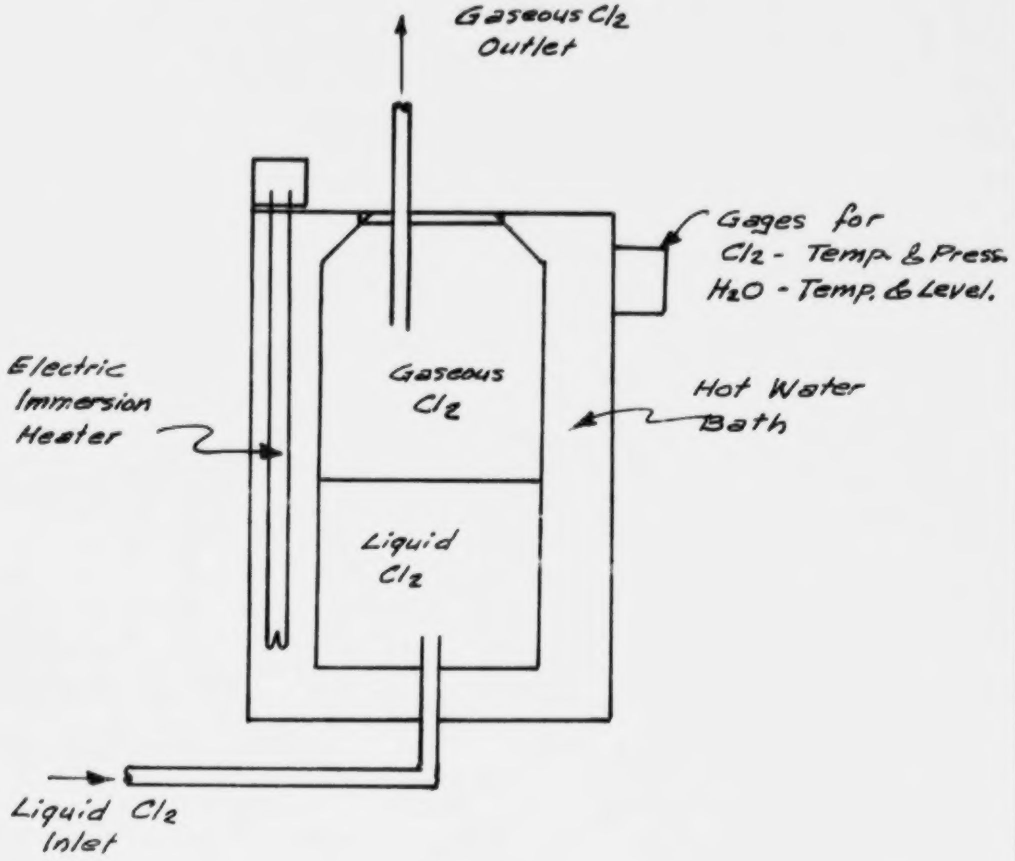
Gaseous Cl_2 Outlet
Gages for
Cl_2 - Temp. & Press.
H_2O - Temp. & Level.
Electric Immersion Heater
Gaseous Cl_2
Hot Water Bath
Liquid Cl_2
Liquid Cl_2 Inlet

FIGURE 4

SCHEMATIC OF A LIQUID EVAPORATOR

NEMHSL, FRD, 807 MAY, 1967

(1959b). Introduction of the liquid to sewage would cause crystalization of the chlorine and water with probably little dissolution resulting. The liquid being 1-1/2 times heavier than water will tend to move downward. Attempts to disperse the liquid with diffuser devices exposes them to clogging by crystal formation.

Application of gaseous chlorine to water or sewage between the temperatures of 49.3°F and 212°F (solubility limit) will not result in crystalization and its related problems. Chlorine gas fed under pressure to water or sewage is termed "direct" or "dry feed" chlorination. The process is quite simple, but due to its drawbacks it is essentially only of historic interest. The gas is motivated by the vapor pressure of the chlorine container and piped through a flow-metering device such as an orifice or flow nozzle and dispersed to the water or sewage through a diffuser. Chlorine control originated with adjustment of the container service valve, a demanding task as the flow rate required varies with discharge. Control problems were improved with the addition of pressure-reducing, pressure-compensating valves, but the problem of adequate dispersion and solution still plagued the method of direct feed. At 20°C, the solubility of chlorine gas in water is 0.7%, thus the gas must be well dispersed in the receiving water. If the receiving water was too cold, chlorine hydrate crystals clogged the diffuser, and frequent diffuser cleaning became necessary. Poor chlorine diffusion or warm receiving water causes chlorine gas to bubble to the surface or become trapped in voids in the piping system. This latter condition causes expensive corrosion problems in valves, pumps, and like appurtenances, AWWA (1951).

The designer should consider under some circumstances inclusion of a check valve within the chlorination system to prevent backup of sewage and/or operating water into the chlorinator. Direct feed of chlorine is too hazardous for the reason that chlorine conducted from the container is under positive pressure and will readily escape if the line is broken. If direct feed must be employed the point of application should be under less than 20 psi pressure, be less than 25 feet from the chlorinating device, and that the chlorinated water or sewage be adequately mixed, Wallace and Tiernan #1.110.

Solution Feed Chlorinators. To overcome the disadvantages of direct feed chlorination, modern chlorinators are generally designed to disperse the chlorine gas into a jet of water to form a concentrated chlorine water solution which is introduced into the sewage. This method is termed "solution feed" and has the advantage of efficiency and control of chlorine dissolution and dispersion. Since more equipment and a solution water is needed this method of chlorination is more expensive than direct feed. The solution water, "injector water," or "operating water" must be supplied under pressure at the rate of over 17 gallons per each pound of chlorine gas (68°F). The solution water delivered under pressure to the injector is designed to cause a vacuum in the chlorine gas line directed into it. When this induced vacuum, by aspiration at the injector, is designed to directly or indirectly control an on-off chlorine inlet valve to the chlorinator, the chlorinator is termed "full vacuum." When the vacuum is broken for example by loss of solution water or loss of solution water pressure, chlorine in the chlorinator is automatically stopped. Solution feed chlorinators without this safety feature are termed "semi-vacuum." Both types are commonly found in sewage plants. Figure 5 presents a schematic diagram of solution feed chlorination operation.

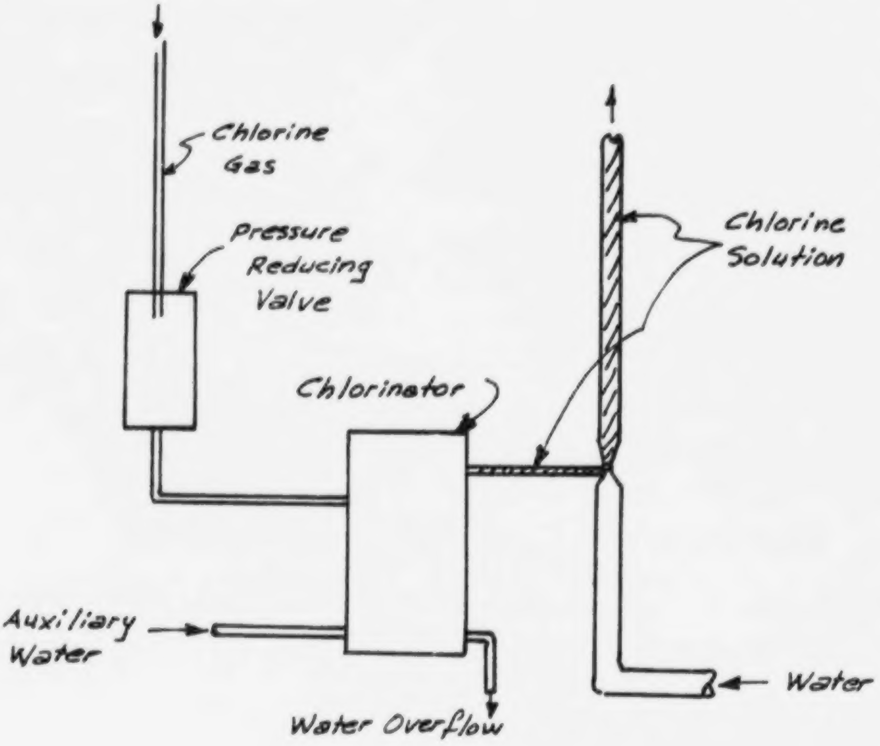
Chlorine Gas
Pressure Reducing Valve
Chlorine Solution
Chlorinator
Auxiliary Water
Water Overflow
Water

FIGURE 5

SOLUTION FEED CHLORINATOR

NEMHSL, FRD, SBA MAY, 1967

Pressure Regulation. On some commercially made chlorinators, an AC or DC heater is attached with the purpose of vaporizing any liquid chlorine that may collect in the piping and be drawn to the chlorinator. Deposition of liquid chlorine and impurities (see Appendix B) in the chlorinator could cause sufficient clogging to necessitate shutdown and purging. There may be difficulty in attaching traps to all chlorinators, however, filters are available on some models.

The chlorine gas entering the chlorinator is under positive pressure induced by the internal pressure of the chlorine container. The entering gas pressure is customarily indicated by a gage on the chlorinator. The gas pressure as described previously will vary with temperature. To achieve a steady gas pressure manufacturers employ pressure reducing and pressure compensating valves to the inlet line of the chlorinator, Fair and Geyer (1959). In some cases these valves may be incorporated into one valve along with the inlet shutoff valve. The orientation and design of the valves varies with the maker and model of the chlorinator.

A common design for pressure reduction and compensation is to direct the chlorine gas into one side of a chamber separated by a membrane or diaphragm from the other side containing water (hydraulic diaphragm) or air (pneumatic diaphragm) under a constant pressure, or atomospheric pressure augmented or stabilized by a coil spring attached to the diaphragm (mechanical diaphragm). Movement of the diaphragm controls the opening for the incoming chlorine gas such that increased chlorine gas pressure will contract the inlet opening and vice versa. This is accomplished in chlorination by the use of a needle plunger attached to the diaphragm and operating within a specially designed gas opening. Chlorinators manufactured before the early '50's often used water under pressure for the opposing pressure in the pressure reducing valves. This was termed "auxiliary water" and was usually required in amounts less than 1 gallon per minute. The auxiliary water had to be fairly clean to prevent clogging or deposition in the valve, which was termed a "hydraulic" valve. The hydraulic-type valves were replaced with spring-loaded diaphragm valves which required no auxiliary water.

To avert possible chlorine leakage occurring within the chlorinator, most makes and models will include safety vents or blow-off lines and pressure relief valves intended to release excessive pressure within the chlorinator, Wallace and Tiernan #5.380. These safety features are generally incorporated within other valves or separate units in the chlorinator piping system.

Measurement and Control of Feed. Once the chlorine gas pressure has been stabilized by the pressure regulating valve, the flow rate must be measured and controlled. In chlorinator design the common flow measuring device had been the orifice up to the advent of the rotameter.

The flow through an orifice plate is a function of the pressure drop and the cross-sectional area of the orifice, and the equation and explanation for this phenomena is in Appendix C.

The rotameter is a vertical, sealed, tapered tube up through which gas is conducted. Within the rotameter is a lightweight float, of one of several shapes ranging from a sphere to a pointed cylinder, which is bouyed up in the tube by the gas entering below. The elevation of the float in the tube indicates the rate of gas flow. The characteristics of the rotameter are such as to permit a nearly linear relation between the flow and the float elevation up the tube and for this reason the rotameter is considered reasonably precise at all flow rates within the range of the rotameter. The length is usually marked to indicate instantaneous gas flow in pounds per day with the float as the indicator.

The method of chlorine flow control will depend upon the make and model of the chlorinator. By employing the orifice, control can be achieved by adjusting the pressure drop across the orifice with a sensitive needle valve or a similar device and meanwhile keeping pressure (or volume) downstream from the orifice constant. Solution feed chlorinators customarily induce a vacuum at the point of solution of the gaseous chlorine and solution water through an "injector" or aspirator. This induced vacuum is extended back up through the chlorinator to the orifice and chlorine flow control is obtained by controlling this vacuum and keeping the pressure upstream from the orifice constant. The pressure drop in this case is from a positive pressure upstream from the orifice to a vacuum downstream.

The rotameter as a flow measuring device does not induce sufficient pressure loss in itself to act also as a controlling device. An orifice regulated by a needle valve could be set in series with the rotameter to induce the necessary pressure drop or a newer technique is to adjust a tapered V-notched plug in a ring, which in a sense is adjusting the orifice's cross-sectional area which controls the pressure drop and the flow.

Rate control on all commercial chlorinators is adjusted with a manual device or knob that also serves as the shutoff and is usually conveniently located on the face of the chlorinator. The term "semiautomatic" control pertains to intermittent or start-stop chlorination with activation coincident with a signal from a source such as a sewage pump or injector water pump. With this type of operation, the dosage rate is usually preset and feeding begins with the reception of the outside signal. With the full vacuum chlorinator, the semiautomatic control is accomplished by shutting off the vacuum or the injector water supply or the pumps delivering the injector water. The signal to start or stop can be activated by one of several methods as for example pump operation, a water level or pressure, or by a timing device.

"Automatic" control is dosage with respect to the variable of one or even two simultaneous parameters. There are several variations of automatic control.

"Step" control is employed where for example a series of pumps are used in different combinations to pump sewage and here feed rate is automatically synchronized to provide dosage for a particular pump or a combination of pumps. In a sense it is dosage in relation to flow. Occasionally the dosage is adjusted with respect to sewage discharge or head as indicated by a level indicating device.

"Program" control is dosage at preestablished rates. Control is usually with respect to time and the rates set on a cam device. A more recent innovation is continuous residual analysis and manual or automatic adjustment of dosage to maintain a minimum chlorine residual and is described in the section on Residual Analyzers, Recorders and Controllers. Signals for chlorinator dosage can be electric, pneumatic, and variable vacuum depending upon the requisites at hand.

The vacuum induced in the solution-type chlorinator by the injector is necessary for chlorinator operation, and like the pressured gas introduced into the chlorinator the vacuum at the outlet must also be regulated. This is usually done by spring-loaded diaphragm valves. In the case of excessive vacuum, vacuum breakers are included with safety air vents to allow air into the chlorinator if the chlorine supply should be discontinued. The bell jar chlorinator was intended to provide a visual inspection of vacuum. The never models tend to employ dial indicating gages. The "full vacuum" chlorinator, or the type where chlorine supply is closed off automatically with loss of vacuum, employs a float in the bell jar attached to an inlet chlorine valve. The water level in the bell jar is sustained by the induced vacuum of the system; therefore, a drop in vacuum produces a drop in water and float level which closes the inlet valve. The necessity of a good quality auxiliary water supply of a few gallons per minute and a provision for drainage can be a drawback in use of the bell jar chlorinator. The trend toward the semivacuum chlorinators is probably due in part to the elimination of the operating water. The makes and models of chlorinators vary in their requirements for inlet or exhaust vents and auxiliary water and drains.

Injectors. The injector of a chlorinator provides the vacuum necessary for solution-type chlorinator operation which introduces and disperses gaseous chlorine into the solution or operating water. The chlorine water solution is discharged from the injector and introduced to the sewage for chlorination. Though injectors are customarily of the aspirator-type, centrifugal injectors have been used and do not require an injector operating water supply but solution water is still required, Wallace and Tiernan #5.150. The operating water is forced through aspirator-type injectors resembling venturis, and a vacuum is developed at the constriction. Since the gaseous chlorine is introduced at the constriction, the vacuum there extends itself back up through the chlorine lines of the chlorinator and pulls the chlorine through to the injector. The injector is necessarily built of materials resistant to the highly corrosive chlorine water and must be designed to withstand the moderately high pressures involved.

Considering the pressure of the operating water and the vacuum of the gaseous chlorine in the injector, provisions for preventing backflow of the operating waters into the chlorinator should be made. Check valves, spring-loaded diaphragms, and drains or combinations of these are employed. Whenever drains are employed, they should be discharged such as to minimize leakage of the gas and undue corrosion of sewage plant drain pipes.

The choice of commercially available injectors will hinge upon an estimate of the chlorine dosage to be applied at the "back pressure" of the operating water. The term "back pressure" describes the pressure of the sewage in relation to the chlorine room floor. It is the pressure of the sewage at the point of chlorine water introduction plus or minus the differences in elevation from this application point to the chlorinator room floor plus friction loss of the chlorine water from injector through the diffuser, Wallace and Tiernan #5.130. The loss in the solution line can be taken as 5 psi, Wallace and Tiernan #5.140. Injectors can be purchased as nonadjustable or adjustable, the latter being employed with the larger chlorinator installations to achieve optimum efficiency for any hydraulic condition encountered. "Centrifugal" injectors, though now of primarily historic interest, were used in chlorination of sewage in open channels.

The flow required to operate the injector is a function of the chlorine discharge and the injector's required pressure. The supply of operating water should be from a reliable source both volume and pressure-wise and free of coarse suspended matter. Where this source might be of questionable reliability, a large pressure storage tank should be employed. When sewage plant effluent is used for operating water, a pressure tank is necessary to provide reliability. When the operating water for chlorination is from a public source there can be a loss of pressure and flow occurring with the opening of faucets and hydrants in the sewage plant causing a drop in chlorine feeding, VanKleeck (1956).

Use of public water also necessitates the precaution against cross-connections occurring in the chlorination system. The supply from public sources should be installed with an air break. Use of pressurized storage tanks for the operating water is perhaps the best alternative. The choice of the use of a potable water supply versus sewage effluent requires a study of the advantages and disadvantages in each case.

TABLE 9

USING TREATED SEWAGE

Advantages	Disadvantages
1) Save on water bill.	1) Chlorine usage could be increased.
2) Supply always available.	2) Could cause clogging in systems with formation of chlorine ice or chloroderivative.
3) Can always go to public supplies.	3) Danger of cross-connections if backup public source is used.
	4) Sewage must be strained and checked periodically.
	5) Intake placed so as to avoid floating solids or bottom deposits.
	6) Wear due to solids in the solution lines.

TABLE 10

INJECTOR OPERATING WATER REQUIREMENTS

ASCE (1963)

Cl_2 Feed Rate in Pounds/Day	Injector Supply (gpm/pound Cl_2/day at 10 psi level pressure)
10-100	0.19-0.055
100-200	0.055-0.053
200-500	0.053-0.050
500-1000	0.050-0.040
1000-8000	0.040-0.032

It is recommended by some manufacturers that the injector water pressure be at least three times that of the sewage at the point of chlorine-water application, Wallace and Tiernan #1.110. Unless under circumstances where head loss would be desirable, it is usually recommended that head loss from the injector to the diffuser or at the point of chlorine water application to the sewage be kept at a minimum. This would involve a careful choice of tubing or piping from the injector with care to avoid too small a diameter and placing the chlorinators as close as possible to the diffusers in order to shorten the conduits.

Chlorinator Capacity. Chlorine dosage is indicated on commercial chlorinators in terms of pounds per day. Individual chlorinators can be purchased with maximum dosages of up to 8,000 pounds per day. The capacity of chlorinators selected is dependent upon the conditions anticipated. The chlorinator capacity should at least meet the legal requirements of dosage be they state or local under all hydraulic conditions. Knowing sewage to be both qualitatively and quantitatively difficult to predict precisely, it is reasonable to be somewhat liberal in a choice of chlorinator capacities. Likewise, the sewage plant should have the chlorination capacity and versatility to chlorinate at different units of the sewage plant, for example, to have the capacity to provide pre- and post-chlorination. Another philosophy is to have the capacity to provide a dose of chlorine that gives total disinfection. Using this philosophy, if legal standards are raised, or for some other reason chlorine dosage must be increased, the chlorination system will have the capacity to meet it, and no major and expensive alterations will be necessary.

As an estimate to the dosage needed the following equation may be used, WPCF (1961):

(max. sewage flow in MGD) (8.34) (chlorine dosage in mg/l) = chlorine dosage in pound/day

The maximum sewage flow depends upon that which can be reasonably estimated from those served by the sewers, be they individuals or industries. As a preliminary step to choice of chlorinator capacity, the dosage in mg/l shown below is based upon the dosing capacity required for a normal sewage under average flow, a modest situation. These dosages are to produce a 2.0 mg per liter residual for disinfection purposes with a minimum contact time of 15 minutes, Upper Mississippi (1954).

raw sewage	25 mg/l
primary effluent	20
trickling filter effluent	15
activated sludge effluent	8
sand filter effluent	6
odor control	20

The addition of industrial wastes might increase the dosage requirement depending upon their character. An estimate of the dosage requirement could be made by laboratory testing a sample of the sewage to determine chlorinator capacity required

Chlorinator Maintenance. Regardless of the claims made for some chlorinators, they are not indestructable. Recently manufacturers have made advances against the problems of wear and corrosion in their products with improved design and use of corrosion resistant plastics and noble metals. Naturally it is good practice to routinely inspect and service all chlorine piping and chlorinators. Some authors have advocated inspection once a day and a complete overhaul of all chlorinating equipment twice a year, Keefer (1940). The chlorinator manufacturers should provide recommended procedures of inspection, maintenance, and lubrication. Parts found by experience or by inquiry to the manufacturers to be particularly vulnerable to breakdown should be stocked at the sewage plant.

Leaks in the chlorine piping or chlorinator piping or chlorinator will result in corrosion to exposed metals. All connections and lines can be checked with an ammonia water swab or a commercial equivalent. Leaks found at threaded joints can be repaired by exposing, cleaning, and coating the joint with a paste of litharge and glycerine and resealing it. Unprotected fittings can be coated with a gasoline-vaseline mixture to prevent corrosion which can also be applied to similar parts of the chlorinator particularly affected by corrosion or during periods when the chlorinator is taken out of service, VanKleeck (1956).

For easy inspection and maintenance, the chlorinator should be situated in the chlorine room. The operator should be sure that as much chlorine as reasonably possible is evacuated from the lines and chlorinator before servicing the machine. Chlorine gas emitted will combine with the moisture in the atmosphere to become a corrosive nuisance, the magnitude of which will depend upon the amount of chlorine gas emitted. Pressure-reducing valves as well as any others suggested for servicing by the manufacturer should be removed and checked, but care should be taken so as to avoid damaging the valves (for example, the valve stem and seat) in removal and replacement, Laubusch (1959c). Any excessive scale can be removed from glass bell jars, floats, or similar parts where scale accumulates. The bell jars should be cleaned with water and washing compound to allow full transparency for which they were intended (Ibid.).

Parts in contact with the dry gas and disassembled for inspection or servicing must be clean and dry before reassembly. They can be washed first with water (to eliminate the water-soluable accumulations), then washed in methanol or carbon tetrachloride and finally completely air dried. Any water strainer provided on the chlorinator can be cleared with diluted hydrochloric acid and air vents must be checked and cleared of any clogging. Places where water can be trapped by plugging or freezing should be avoided, VanKleeck (1956).

Needless to say, all parties concerned with chlorine handling should use materials or equipment in contact with chlorine that are free of impurities or those that will not react with chlorine to form impurities. The sewage plant operator should be conscious of the cleanliness of his chlorinating system and of precautions necessary to avoid any chlorine contamination. Chlorine equipment, for example, should be cleaned only with safe solvents such as methane derivatives, chloroform, wood (methyl) alcohol, or carbon tetrachloride, AWWA (1951). Other precautions are mentioned by Laubusch (1959a):

> "Published references suggest that the majority of such difficulties (clogging of chlorination system by chlorine contaminants) are attributable to maintenance errors or negligence at the feeding facility. For example, atmospheric moisture may enter a system during shutdown; lubricants and cleaning solvents that can react with chlorine may not be properly removed before the system is returned to service; lubricants and packing materials may be forced into the system by excess tension on packing glands; protective diaphragms of pressure gages may become ruptured and discharge diaphragm oil into the system; or deposition of several months' chlorine flow may suddenly be redissolved by condensing droplets of liquid chlorine and deposited at the first point of gas expansion. Clearly then, there are numerous opportunities for chlorine contamination incident to the feeding process."

Stand-by Chlorinators. The Joint Committee on Chlorine Supplies was founded in 1951 to resolve the chlorine supply problem. It consisted of representatives from the AWWA, the Conference of State Sanitary Engineers, the USPHS, and the Federation of Sewage and Industrial Wastes Association. The following recommendations for stand-by chlorinators in view of public health protection were expressed and fully quoted because of their significance, Joint Committee (1953):

> "In the small plant, whether it be for water supply, sewage disposal, or industrial waste treatment, requiring only one chlorinator for normal operation, one additional chlorinator should be provided for emergency situations. The size of the emergency unit should equal in capacity that of the basically required unit. Installations requiring two, three, or more chlorinating units in operation, stand-by needs should be met by providing a duplicate of the largest unit of the group to provide one unit more than is required for normal maximum demand. Consideration should be given in the original design to the desirability of using several small units providing flexibility not available with one or two large units.
>
> Several general comments are made with regard to stand-by equipment. Of equal importance to provision of stand-by equipment is the regular frequent servicing of all chlorinating equipment. Any stand-by equipment should be kept in perfect running order at all times. Borrowing of parts from stand-by equipment should not be permitted. A definite schedule of chlorinator use should include frequent routine operation of any stand-by equipment. Reliance on emergency equipment maintained by state health departments should not be considered as serving in lieu of stand-by equipment located at the installation itself. Possible availability of equipment from manufacturers should not be considered as meeting stand-by equipment needs. Knowledge of types of equipment used in nearby plants might prove of limited service at times when it might be possible to borrow a part of a chlorinating unit to replace a damaged or broken part.
>
> Many chlorine feeders employed in the treatment of water supplies, sewage or industrial wastes are dependent on power to operate pumps or provide auxiliary water or air pressure used in connection with the feeders. Where there is also need for power to produce the flow of water, sewage, or industrial wastes that is to be treated, the power for the chlorine feeder may be derived from the same source; an interruption of the flow is timed with

> the interruption of the chlorination. However, where the flow of the liquid to be treated is by gravity or where the source of power to produce the flow is from some other source than the source used to operate the chlorinator, failure of the electric or other power used to operate a chlorinator may cause interruption of the chlorine disinfection of the flow. A common practice is to install hydraulic pumps along with electric power to operate chlorinators, with the hydraulic pumps cutting in when electric power is interrupted.
>
> In the air-operated chlorinators, air is usually provided by small electrically operated compressors. Interruption of the flow of compressed air through power failure will shutdown the chlorinators. To prevent such interruption of chlorination, an auxiliary source of compressed air is required. This may be provided by a gasoline engine driven auxiliary compressor or by a reserve supply of cylinders of inert gas, such as carbon dioxide. A minimum of two cylinders of carbon dioxide in service at the same time on each chlorinator is required to operate one chlorinator for a minimum of 10 hours. The use of high-pressure carbon dioxide presents an operational hazard. Such an installation should be made and operated only in accordance with the recommendations of the chlorinator manufacturer."

Diffusers

Chlorine solution diffusers are designed to efficiently distribute the chlorine solution throughout the sewage. The design encompasses a consideration of corrosion, clogging, and strength to withstand the hydraulic stress anticipated. They should be designed for easy removal to allow inspection and servicing without halting or affecting sewage plant operation, Wallace and Tiernan #5.270.

In situations where "direct feed" chlorination is employed, a primary consideration is incomplete solution of the chlorine in the sewage and bubbling off of the gas. For this reason it is usually recommended to place the diffuser at least 4 feet below the surface, Keefer (1940). Any escaping gas will be moist and corrosive, and situations where this could cause damage should be avoided. This means no buildings should be located over the point of application, VanKleeck (1956a). If the sewage is not chlorinated in a closed conduit, the channel top could be sealed and periodically checked for leaks by an ammonia water swab. Gas leakage might be rectified by deeper immersion of the diffusers or by replacement with more efficient diffusers. The cylindrical porous-stone diffuser (the largest having a maximum capacity of 75 pounds per day) is claimed by some to be the most efficient available, which if used in open wells or flumes can be employed in grids of six diffusers with up to a capacity of 300 pounds per day, Wallace and Tiernan #5.200. Leakage, corrosion in metal conduits, and diffuser clogging by chlorine hydrate (VanKleeck, 1956a) are problems often encountered in "direct feed" chlorination, therefore, this mode of chlorination is discouraged unless the conditions for "solution feed" are not possible.

Solution feed diffusion in open channels, often encountered at the smaller sewage plants, may be accomplished by submerged spray nozzels, consisting of rubber lined and covered perforated pipe anchored either vertically or horizontally in the channel (Wallace and Tiernan #5.270) or simply by submersion of plastic pipe drilled and fitted on the site.

Chlorine solution discharged from up to 1 inch diameter hoses into sewage pipes up to a 24 inch diameter is often accomplished with a silver solution tube using a 1 inch corporation cock attached to the sewer line (Ibid.). The diffuser tube can then be easily installed or removed even when the sewage in the pipe is under pressure. Two or more similar diffusers can be set at different angles in the sewage pipe for higher dosages or better diffusion. Situations of high sewage flows and high chlorine solution discharges are often handled with a fixed rubber coated steel diffuser extending across the diameter of the sewage pipe. The diffuser should be designed to provide good dispersion of the chlorine solution in the sewer pipe, but to be certain of good mixing, an additional mixing device after the diffuser might be necessary. Design of diffusers involves the orientation, size, and friction loss of perforations, and a simple means of replacing or inspecting the diffusers.

Hypochlorination

Hypochlorites. Of all the chlorine compounds available, calcium and sodium hypochlorites are the ones most used in sewage treatment.

Calcium hypochlorite is usually used in water and waste treatment in a refined state more commonly called "high-test hypochlorite." The three firms currently producing high-test hypochlorites each have their own technique of production. The Pennsalt Chemicals Corporation*, for example, sells a high-test hypochlorite called "Perchloron," which is produced by filtering, pressing, breaking, and drying a special chlorinated limeslurry solution, Encyclopedia (1949). This product, like all high-test hypochlorites, is sold either as a grain or a powder. Other high-test hypochlorites currently marketed are sold under the trade name of Chlor-Tabs (Pennsalt Chemicals Corporation), HTH (Olin Mathieson Chemicals Corporation), Pittchlor and Pit-Tabs (Columbia-Southern Chemical Corporation). The price of chlorine compounds may be

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*Mention of trade names does not constitute endorsement.

4 to 10 times that of liquid chlorine and the high-test hypochlorites all have at least 70% the oxidizing power of an equal weight of liquid chlorine.

Unlike the high-test hypochlorite, sodium hypochlorite is made by a multitude of manufacturers offering products of widely varying qualities, Laubusch (1960a). Although electrolysis can be employed to produce sodium hypochlorite, the customary procedure is to chlorinate a solution of caustic soda. The product is sold as a liquid and can be purchased in a variety of containers.

Chlorinated lime, also called bleaching powder or chloride of lime, is now rarely used in sewage treatment due to the advent of the high-test hypochlorites. It is usually prepared by exposing hydrated lime to a mixture of chlorine gas and air which produces a product of indefinite composition containing mostly calcium oxychloride ($CaOCl_2$).

Though it is not commonly used in sewage treatment, chlorine dioxide is mentioned because of its powers of disinfection. Gaseous chlorine dioxide is usually generated at the site of application by adding chlorine to flake sodium chlorite.

Dry Feed. Dry feed hypochlorination, as the term implies, is the addition of solid hypochlorite to water or sewage, but not all of the common hypochlorites are suited for dry feed application. Sodium hypochlorite, for example, is commercially available only as a liquid. Chlorinated lime being highly hygroscopic, corrosive, and deteriorative in air, is best not applied by a dry feed hypochlorinator. Thus, dry feed is better suited for calcium hypochlorite or the high-test hypochlorite than for other hypochlorites, Laubusch (1960a).

Dry feed technically may include hand application, dissolution of hypochlorite pellets in a perforated container set in the water or sewage, up to sophisticated gravimetric and volumetric feeders. However, since all hypochlorites are to a degree deteriorative and hygroscopic, the volume and specific gravity of solid hypochlorites are not constant and use of gravimetric and volumetric feeders must be done with discretion. Dry feeders are available commercially, although their use in sewage treatment is rare.

Bleach Solution Hypochlorination. Experience with hypochlorination of water and sewage has indicated that hypochlorites can be conveniently and simply applied by being dissolved and diluted in what is called a "bleach" solution. This bleach solution of known "available chlorine" content is then measured and dispersed into the water or sewage as required. The hypochlorites are readily soluble in water, even more so than chlorine gas. Calcium hypochlorite, for example, at 0°C is soluble in water up to 218,800 mg/l (21.9%) and at 40°C up to 234,000 mg/l (23.4%). The concentrations of the bleach solution applied to sewage are considerably lower in concentration than this. That recommended for high-test hypochlorite is in the realm of from 1 to 2 percent. The volume of bleach solution required is a function of the volume of sewage treated, bleach solution dosage, and the strength of the bleach solution as shown from the following equation (Ibid.).

Gallons of standard bleach solution required =

$$\frac{(\text{sewage treated, gal.})\ (\text{chlorine dosage, mg/l})}{(10{,}000)\ (\%\ \text{available chlorine in bleach solution})}$$

6.2a

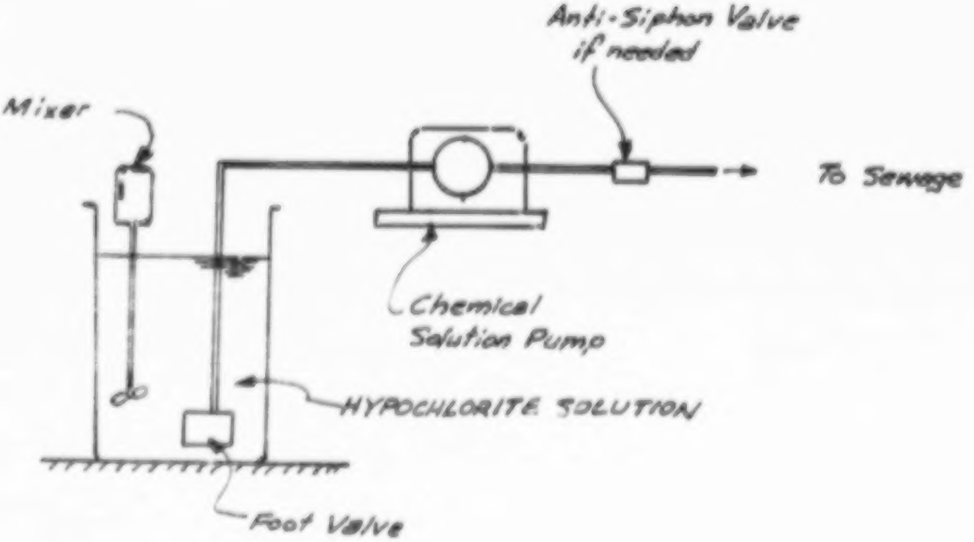

Anti-Siphon Valve
if needed
Mixer
To Sewage
Chemical
Solution Pump
HYPOCHLORITE SOLUTION
Foot Valve

FIGURE 6

TYPICAL HYPOCHLORITE
FEEDER

NEMHSL, FRD, SO7 MAY, 1967

Some hypochlorites have the disadvantage of producing a sludge when dissolved in water with calcium carbonate and other inert materials. To avoid excessive sludge formation, and possible sludge carry-over to the hypochlorite pumping device or appurtenances subject to clogging, the amount of hypochlorite dissolved in the bleach solution is generally kept low. For example, excessive sludge will accumulate if over 5 pounds of chlorinated lime or 11 pounds of high-test hypochlorite is dissolved in each 10 gallons of water. Sodium hypochlorite being available as a liquid produces essentially no sludge, VanKleeck (1956). It has been recommended that the uppermost liquid of the bleach solution be decanted for use to avoid clogging by the sludge (Ibid.). Bleach solutions may also be premixed, settled, and the supernatant decanted or siphoned off for application, Laubusch (1961).

The amount of "available" chlorine use can be determined by calculating the pounds of "available" chlorine per inch of bleach solution container depth, and thereafter measuring the drop of solution level per hour or day, VanKleeck (1956). Bleach solutions are oxidants, corrosive and are best prepared in containers not subject to corrosion such as earthenware crocks or rubber lined or plastic barrels, Ehlers and Steel (1958). To preserve most of the activity in the bleach solution preparation should be done in a cool dark area of the sewage plant, preferably an area free of direct sunlight.

Feeders. The simplest way of applying chlorine bleach solution may be by dribbling it into the sewage at a constant rate through a valve attached to a solution container. To obtain somewhat more assurance of constant application an orifice and a constant head bar could be included. In order to achieve more accurate dosage control and reliability more sophisticated means are required, which should be a requisite of sewage chlorination. The commercial hypochlorinators that are available may be classified as positive displacement feeders, orifice or venturi feeders, or as suction-type feeders, Moore (1951). Figure 6 presents a typical hypochlorite feeder setup.

Positive Displacement Feeders. The positive displacement feeder can be either a diaphragm pump or a piston-type pump. This complex feeder, claimed to be the most accurate of hypochlorinators, is especially adaptable to situations where the hypochlorite must be pumped against pressure, where hypochlorite must be fed in proportion to sewage flow, where hypochlorination must be continuous, and where dosage rates are high, Laubusch (1961). These feeders are usually activated by electric motors, although other types of power for emergency situations are also available. Control of dosage can be done manually or in some cases automatically in proportion to sewage flow. As mentioned previously, the use of hypochlorites for sewage chlorination is usually confined to the smaller plants where mechanical sophistication is neglected but so often highly desirable.

Positive displacement feeders are easily regulated within their specified range. Where more capacity may be desired the plant operator could consider either using a stronger bleach solution, changing the stroke length, changing stroke speed, and if available, using more heads of a multiple head pump.

Diaphragm feeders are obtainable commercially in a wide variety of makes and models with simplex, duplex, or even triplex heads. Dosage capacities are likewise variable, delivering up to 24 gallons per hour dosage at 100 psi dosage pressure. Where the hypochlorinator must be pumped into a low or negative head system an antisiphon device should be installed with this type feeder (Ibid.).

Piston-type or plunger-type feeders are available in a variety of capacities up to about 60 gallons per hour dosage and pressure up to over 5,000 psi (Ibid.). These feeders can be activated by gasoline, air, or electric power supplies to meet nearly any emergency situation.

Pressure Differential Feeders. The pressure differential feeder, usually of simpler construction and cheaper cost than the positive displacement feeder, measures the bleach solution flow by pressure differential induced by an orifice, venturi, or similar device and control is achieved by varying the pressure differential. Some models are available with up to 20 gallons per hour dosage for up to pressures of 100 psi (Ibid.).

Suction Feeders. This type feeder is apparently best adaptable to situations of low discharge or intermittent dosages, for example, domestic or low flow industrial treatment. This feeder employs suction, gravity, or siphonic action to draw the bleach from a container to the water or sewage which requires connection to a pumped flow, thus limiting this type of unit to water supply in general.

Hypochlorinator Selection. The multitude of makes and models of commercially available hypochlorinators makes it easy for the designer to satisfy his requirements but more difficult to choose. Choice of a hypochlorinator, as suggested by Laubusch (1961) should involve the following considerations:

1. Job requirement
2. Treatment objectives and purposes
3. Scope of treatment
    a) continuous
    b) intermittent
4. Flow ot be treated
    a) quantity
    b) quality
    c) fluctuations
5. Chemical requirements
    a) amount
    b) kind
    c) availability
6. Available means of actuating feeder
    a) water
    b) air
    c) electric power
    d) etc.
7. Point of application
    a) open stream or basin
    b) pump intake or discharge
    c) pressure main
    d) etc.
8. Pressure at the point of discharge
    a) positive
    b) negative
9. Control desired
    a) manual
    b) automatic off-on
    c) proportional
10. Degree of supervision available
11. Amount and kind of maintenance required to insure satisfactory feeder performance.

12. Costs
    a) initial
    b) operating
    c) maintenance

The hypochlorinator capacity will among other things be a function of the treatment requirement and strength of the hypochlorite solution (or bleach volume) (Ibid.). Conversely, in some cases the capacity range of the available hypochlorinators may dictate to some degree the strength of the bleach solution. For example, small sewage flows requiring small dosages of hypochlorite may require a highly diluted bleach to provide enough volume for the minimum pumping rate of the hypochlorinator, and likewise large sewage flows requiring high dosages of hypochlorite may require a strong bleach solution at the feeder's peak dosage rate to meet the chlorine requirement.

Mixing. The importance of dispersing the hypochlorite bleach solution throughout the sewage cannot be stressed enough. The procedures to provide for proper dispersion would be the same as discussed previously in the mixing of chlorine and sewage section.

Hypochlorinator Maintenance. Laubusch (1961) has recommended that hypochlorinators be torn down and inspected at least semiannually. Hypochlorinator parts such as needle control valves, small orifices, venturi throats, ball check valves, and inlet and outlet poppet valves are susceptible to clogging, especially when the water used may contain hardness, iron, minerals, particulate matter, and the bleach solution has calcium in suspension. These parts should be brush-cleaned using a 5% muriatic acid or an acetic acid solution. As a preventive measure the operator could also give the hypochlorinator (including the bleach solution strainer) a daily flushing (or as often as necessary) with clear water or he may consider using a sequestering agent such as sodium hexametaphosphate where the problem is severe. Worn or damaged parts should be replaced and a supply of replacement parts should be made available (especially poppet valves, valve seats, diaphragms, O-rings, feeder tubes or those parts recommended by the manufacturer), and lubrication should be executed as recommended by the manufacturer.

Stand-by and Alarm. The recommendations set forth in the "Report on Recommended Procedures in the Use of Chlorine at Water and Sewage Plants," Joint Committee (1953), might well apply to the situation for stand-by hypochlorinators. In the small sewage plants, where hypochlorinators are most likely to be used, one hypochlorinator may handle the daily sewage requirement, however, the recommendation set forth from the above reference would still require that another unit be available for "emergency situations."

Alarm systems are available which would warn the plant operator or responsible personnel of the failure of the hypochlorination system. An alarm could be activated by stoppage of the hypochlorite, by a certain low level of the bleach solution, by a power failure, or by a certain low chlorine residual level of the sewage. The particular alarm system used would be determined by the particular sewage plant layout as well as human and financial considerations.

CHEMISTRY OF CHLORINATION

Elemental Chlorine

Chlorine derived its name from the Greek word "chloros" meaning greenish-yellow, a color description of chlorine gas. At room temperature and atmospheric pressure chlorine exists as a gas. Approximately 5 cubic feet of the gas will condense into a pound of liquid chlorine below -34.6°C, Hodgman, Weast, and Selby (1959). Liquid chlorine is heavier than water having a specific gravity of 1.468 at 0°C (3.617 atmospheres pressure) compared to 4°C water. Gaseous chlorine is likewise heavier than air with a relative vapor density (air = 1) of 2.482 at 0°C and 1.0 atmosphere pressure, Laubusch (1963).

Neither chlorine gas or liquid chlorine are explosive or flammable in air but can react violently with certain substances in a manner like that of oxygen, Laubusch (1963). The gas has a threshold odor of 3.5 ppm by volume and 1,000 ppm will kill most animals in a short time, Chlorine Institute (1959b). Chlorine gas, often considered a "war gas" attacks the respiratory tract. Low concentrations will cause irritation of the muccus membranes of the respiratory system with usually no permanent damage to the lungs, however, in severe cases the primary concern is the onset of pneumonia and like secondary complications, Hardie (1959). For this reason sewage plants must have the necessary safety features and procedures available in the case of chlorine leakage. These might include gas masks conveniently set outside the chlorine room, windows to permit easy inspection of the chlorine room, chlorinator room, or storage room. Alarms are available which continuously monitor the chlorine room atmosphere for chlorine gas. In the event of leakage which cannot be stopped, it may be possible to discharge leaking chlorine into a alkaline solution and the quantities required are shown below in Table 11.

TABLE 11

RECOMMENDED ALKALINE SOLUTION FOR ABSORBING CHLORINE
(Joint Committee, 1953)

Chlorine Container	Caustic Soda (1)		Soda Ash		Hydrated Lime (2)	
	Lbs.	Water gal.	Lbs.	Water gal.	Lbs.	Water gal.
100#	125	40	300	100	125	125
150#	188	60	450	150	188	188
1 ton	2500	800	6000	2000	2500	2500

(1) 100%

(2) Hydrated lime solution must be continuously agitated with vigor while chlorine is to be absorbed.

The production of hypochlorites are an example of the reaction of chlorine with alkalies and alkaline earth metal oxides (Chlorine Institute, 1959b) forming compounds which retain some of the oxidizing power of chlorine.

Chlorine reacts with organics to form chlorinated derivatives and hydrochloric acid (HCl). Some of these reactions, such as with hydrocarbons, alcohols, and ether, proceed with explosive violence, Laubusch (1963). Chlorine has a strong affinity for hydrogen, and under the proper concentrations and circumstances need only sunlight to react explosively, Frey (1959). Chlorine oxidizes hydrogen sulfide to produce hydrochloric acid and free sulfur while controlling hydrogen sulfide odors in sewers and sewage treatment plants.

$$H_2S + Cl_2 \longrightarrow 2\ HCl + S$$

The reactivity of chlorine as a gas as well as in the form of a hypochlorite, demands that caution be taken with certain compounds that might be brought in contact with them. Of particular concern are turpentine, ether, anhydrous, ammonia, finely divided metals, hydrocarbons, and other flammable materials, Laubusch (1963).

Hydrolysis of Chlorine Gas

As shown on Figure 7, the solubility of chlorine gas in water is low. This curve is based upon laboratory analyses, but practical solubility is even somewhat less. At normal water temperatures, the solubility is less than 1%. Below 9.6°C (49.2°F) chlorine gas and water will form solid chlorine hydrate ($Cl_2 \cdot 8H_2O$) often referred to as "chlorine ice." Chlorine gas is insoluble in water at or above 100°C. Based on this information, the chlorine solution formed from chlorinator injectors would hardly be expected to exceed a 10,000 mg/l residual.

As the chlorine gas is drawn into the injector by the injector water forming the solution water at the injector discharge, the following chemical reaction theorectically occurs, Moore (1951):

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

In the absence of sunlight and at ordinary temperatures this reaction is quite rapid, reversible, and is completed within a few seconds, Quagliano (1958). In a strong light or in the presence of ultraviolet light the following equation occurs (Ibid.):

$$2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2 \uparrow$$

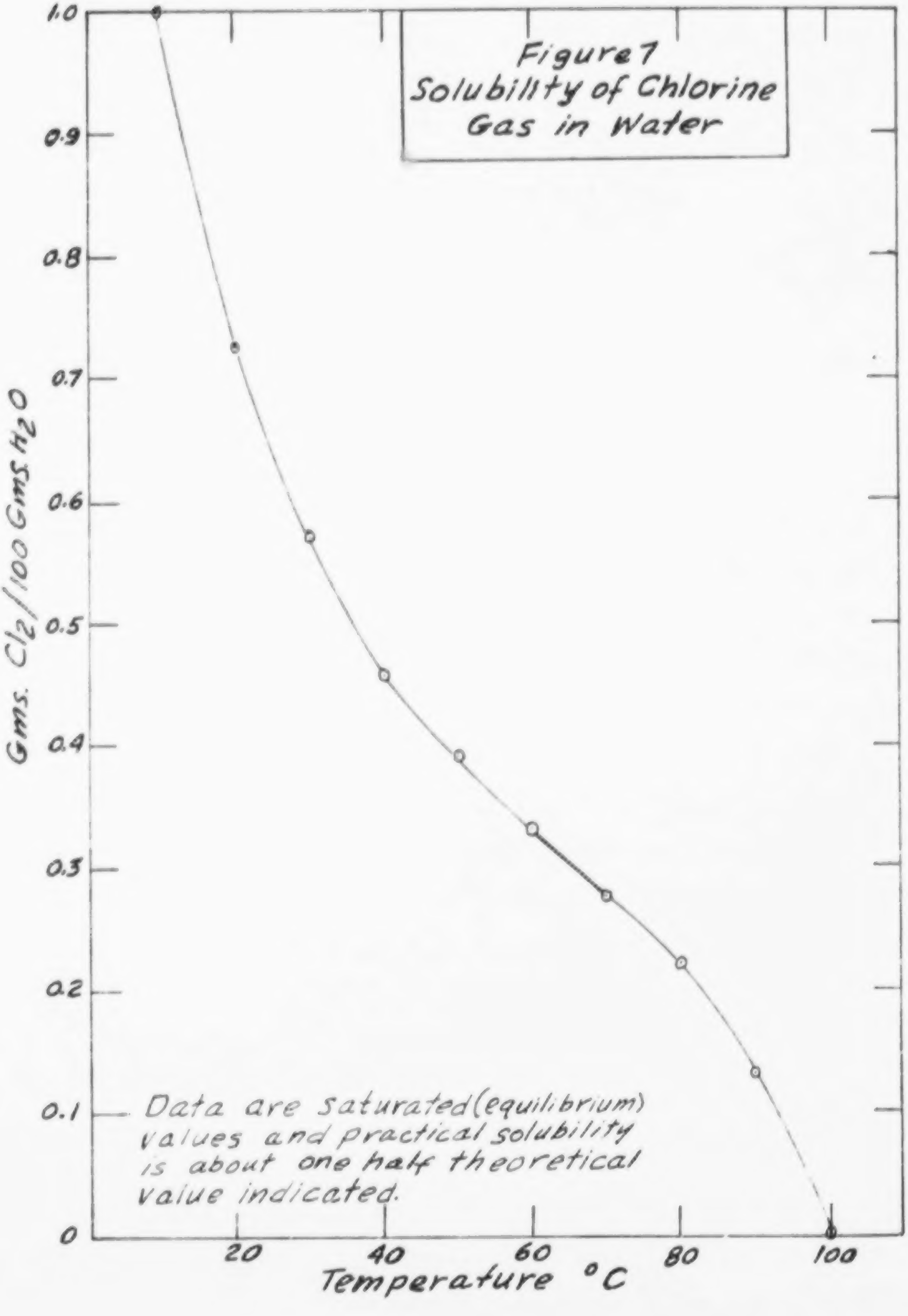


Figure 7
Solubility of Chlorine
Gas in Water
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
20
40
60
80
100
Gms. Cl_2/100 Gms H_2O
Temperature °C
Data are saturated (equilibrium) values and practical solubility is about one half theoretical value indicated.

The formation of hypochlorous acid (HOCl) and hydrochloric acid (HCl) accounts for the highly corrosive character of moist chlorine gas. Hypochlorous acid, of particular germicidal interest, is considered a weak acid.

The equilibrium equation of chlorine gas hydrolysis in the absence of strong light is stated as follows, Moore (1951):

$$\frac{(HOCl)\ (H)\ (Cl^-)}{(Cl_2)} = Kh$$

K_h* at 25°C is 4.5×10^{-4} $(mols/l)^2$, Fair and Geyer (1959), and the concentration of each term in the equation has the dimension of mols/liter. When the pH is above 3.0 and the chlorine residual is less than 1,000 mg/l the amount of Cl_2 in the solution water will be essentially too small to be measurable. Therefore, sewage plants using injector water of public water qualities will produce a solution water containing essentially all its chlorine in a form other then Cl_2.

It should be realized that unless chlorine is hydrolyzed in the purest water, some chlorine will not go to HCl and HOCl but will be used up in other side reactions such as with alkalinity or organics. These side reactions will be discussed later.

The chlorine hydrolysis products of HCl and HOCl will themselves essentially dissociate instantaneously in reversible reactions, Fair and Geyer (1959):

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

---

*K_h is the solubility constant.

Hydrochloric acid being a strong acid is nearly completely dissociated in dilute solutions. The hypochlorous acid, however, being a weak acid dissociates as a function of the solution pH and temperature. The dissociation of HOCl is of particular interest due to the difference in germicidal action between it and its dissociation product, OCl^-. The germicidal agents of chlorine or its products apparently are not completely yet understood. The germicidal action has been attributed to HOCl, HCl, nascent oxygen or free chlorine which could be formed by the following equations, Frobisher (1957):

$$HOCl + HCl \longrightarrow H_2O + Cl_2$$

$$2HOCl \longrightarrow 2HCl + O_2$$

$$2Cl^- + H_2O \longrightarrow 2HCl + \tfrac{1}{2}O_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

The dissociation of the hypochlorous acid may be stated by the following equation and table for various temperatures, Fair and Geyer (1959).

$$\frac{(H)\ (OCl^-)}{HOCl} = K_i$$

°C	0	5	10	15	20	25
$K_i \times 10^8$ mols/l	1.5	1.7	2.0	2.2	2.5	2.7

The relative portion of OCl^- and HOCl in pure water at 0°C and 20°C are shown on Figure 8, Moore (1951).

It is evident that between 0°C and 20°C temperature has a minor effect on the dissociation of hypochlorous acid, whereas pH is highly significant. Note that under acid conditions, especially below pH 6.0, the HOCl will predominate whereas over a pH of 9.0 the OCl^- will predominate.

Hydrolysis of Hypochlorite

The hydrolysis of hypochlorites results in essentially the same products as for the hydrolysis of chlorine gas. The hydrolysis of chlorinated lime, which consists primerily of calcium oxychloride ($CaOCl_2$), is hydrolyzed as follows, AWWA (1951):

$$2CaOCl_2 + H_2O \rightleftharpoons Ca(OCl)_2 + CaCl_2 + H_2O$$

The calcium hypochlorite formed ($Ca(OCl)_2$) is in turn ionized to the hypochlorite and calcium ions, Wallace and Tiernan #5.130.

$$Ca(OCl)_2 + H_2O \rightleftharpoons Ca^{++} + 2OCl^- + H_2O$$

As in the case of chlorine gas hydrolysis, the hypochlorite ion will combine in a reversible reaction with a hydrogen ion forming hypochlorous acid.

$$H^+ + OCl^- \rightleftharpoons HOCl$$

As mentioned previously the proportion of OCl^- and HOCl formed will depend greatly upon pH.

The hydrolysis of sodium hypochlorite is similar to the hydrolysis of chlorine gas:

$$NaOCl + H_2O \rightleftharpoons Na^+ + OCl^- + H_2O$$

$$H + OCl^- \rightleftharpoons HOCl$$

The hydrolysis of the hypochlorites tends to raise pH and the actual proportion of OCl^- and HOCl formed will depend upon the pH of the solution after addition of the hypochlorite and not the original pH of the water, Moore (1951). Hydrolysis of chlorine gas tends to lower the pH of the chlorine solution, with a tendency toward HOCl formation. As a consequence, if sufficient quantities of chlorine gas and hypochlorite are hydrolyzed in separate volumes of water or sewage to change the resultant pH, the chemical and germicidal action induced in each volume may be expected to differ.

Available Chlorine

The amount of a chlorine compound applied to sewage is based upon the weight of chlorine gas that would have the equivalent oxidizing power of a unit weight of the compound actually applied. Since the dosage is based upon oxidizing power, any oxidizing agent may be equated to the chlorine gas regardless of whether or not it actually contains chlorine. This measure of oxidizing power is termed "available chlorine," and unfortunately confusion often arises due to the interpretation that it is a measure of the chlorine content of the compound. Potassium permanganate, for example, contains no chlorine but it does have an "available chlorine" content or oxidizing strength. In many pure chlorine compounds, the actual amount of chlorine present does not necessarily agree with the "available chlorine" content as illustrated in the following adapted Table from Moore (1951):

TABLE 12

compound	mol weight	mols of "equivalent chlorine"*	% Cl_2 by weight	
			actually present	"available chlorine"
Cl_2	71	Cl_2	100.0	100.0
$CaClOCl$	127	Cl_2	56.0	56.0
$NaOCl$	74.5	Cl_2	47.7	95.4
$Ca(OCl)_2$	143	$2Cl_2$	49.6	99.2
NH_2Cl	51.5	Cl_2	69.0	138.0
$NHCl_2$	86	$2Cl_2$	82.5	165.0
Cl_2O	87	$2Cl_2$	81.7	163.4
$HOCl$	52.5	Cl_2	67.7	135.4

---

*Number of mols of chlorine that would have an oxidizing capacity equivalent to 1 mol of the compound.

"Available chlorine" is stated as a percent either by weight or by volume (trade) of the compound in question and the equations for both expressions are given as follows, AWWA (1953).

$$\text{Volume or trade percent} = \frac{\text{grams available chlorine per liter}}{10}$$

$$\text{Weight percent} = \frac{\text{volume percent}}{\text{specific gravity of solution}}$$

The test for "available chlorine" as stated by the American Water Works Association (1953) is slightly altered for solid hypochlorite (chlorinated lime and calcium hypochlorite) or hypochlorite in the liquid form (sodium hypochlorite) and can be found in Appendix E.

Dosage Calculation (Hypochlorite)

Calculation of the amount of hypochlorite required to treat a given volume of sewage is based upon the oxidative capacity of the hypochlorite stated in terms of chlorine gas, the units being pounds of "available chlorine." One pound of "available chlorine" of a particular compound then is equivalent only to the oxidizing power of one pound of chlorine gas, and is not necessarily equivalent to one pound of the compound nor does it mean that the compound contains one pound of chlorine. For example, one pound of 70% "available chlorine" high-test hypochlorite is equivalent in oxidizing power of 0.7 pound of chlorine gas. Thus, a sewage plant requiring a total of 70 pounds of chlorine gas a day would require 100 pounds of 70% "available chlorine" high-test hypochlorite.

As indicated by AWWA (1953), the test for percent "available chlorine" of high-test hypochlorites (calcium hypochlorite) is given as percent by weight. Chlorine compounds such as sodium hypochlorites might be obtainable only as a liquid. In this case the "available chlorine" is stated in terms of a volume percent. For example, a commercial sodium hypochlorite may be stated to have 15% "available chlorine," or 150 grams per liter (1.25 pounds per gallon) of "available chlorine." A sewage volume requiring 70 pounds per day of chlorine gas would require 56 gallons per day $\left\{\frac{70\#/\text{day}}{1.25\#/\text{gal.}}\right\}$ of sodium hypochlorite.

To achieve better dispersion and application control of hypochlorites, they are usually diluted into what are called "bleach solutions of from 1 to 15% 'available chlorine'" and the prepared "bleach solutions" are applied to the sewage. The preferred "bleach solution" strength among other factors will depend largely upon the feed rate employed and the storage capacity available for the solution, VanKleeck (1956).

Requirement, Demand, and Residual

The formal definition of chlorine requirement as stated in the 11th Edition of Standard Methods is as follows, APHA (1962):

> "Chlorine requirement is defined as the amount of chlorine which must be added per unit volume of sewage to produce the desired value of residual chlorine after a stated contact time."

In sewage treatment, the term "chlorine requirement" has superseded the narrower term of "chlorine demand" which stated a contact time (15 minutes) and a residual (1.0 mg/l). The former term thus requires a statement of the residual chlorine concentration, observed, the contact time, and the residual chlorine test employed. The chlorine requirement test is outlined in Appendix D.

In water treatment two types of chlorine residuals, free and combined, are recognized. The free chlorine residual is intended to indicate the concentration only of the hypochlorite ion (OCl^-) and hypochlorous acid ($HOCl$). The combined residual chlorine as defined by the AWWA (1951) is:

> "That chlorine existing in water in chemical combination with ammonia or organic nitrogen compounds..."

The free chlorine produced in the chlorine solution water soon dissipates itself in numerous side-reactions with sewage. The practice is to disregard free chlorine residual and measure only the combined and in general no attempt is made to obtain a free residual in sewage.

Activity in Sewage

Some important factors of sewage chlorination to consider are that the hypochlorite ion as well as the hypochlorous acid are oxidants prone to enter into side reactions with sewage constituents. This means that the original chlorine introduced into sewage will in time lose much of its oxidizing "punch." Some will be reduced to the chloride ion (Cl^-). Cl_2 in an acid solution will have a strong tendency to go to Cl^- rather than to the HOCl, and likewise in basic solutions it has nearly equal tendencies to go to Cl^- as well as OCl^-, Quagliano (1958).

The Cl_2 that does go to $HOCl$ and OCl^- in water plus any free Cl_2 will combine directly with organic and inorganic matter through oxidation. Coagulation and precipitation or a change in the physical state of organics may take place, AWWA (1951).

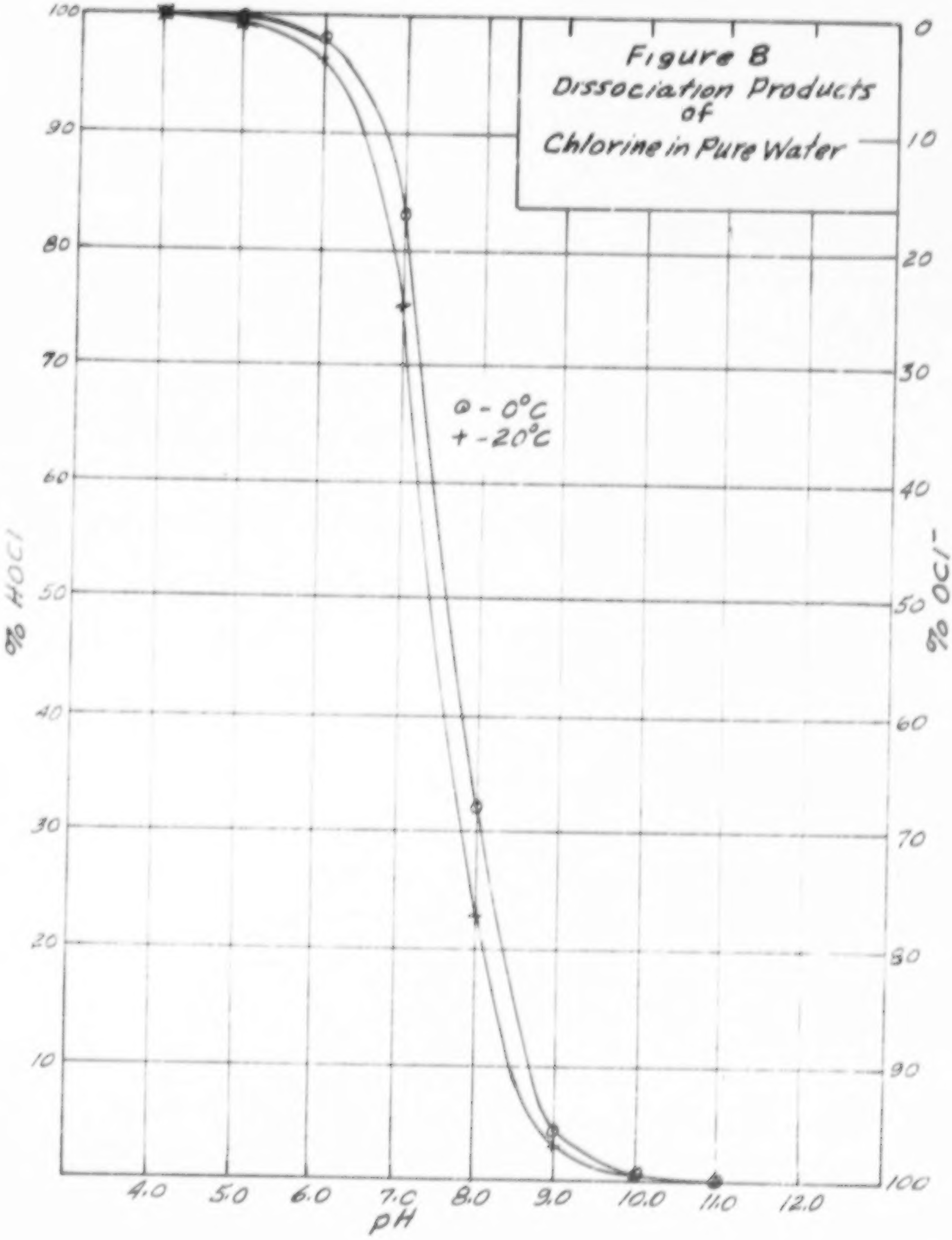


Figure 8
Dissociation Products
of
Chlorine in Pure Water

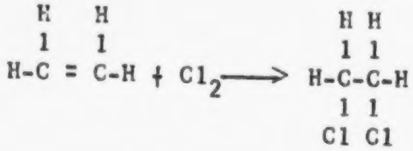
The intensity of these chlorine side-reactions can be measured by the oxidation-reduction potential (ORP) in volts. The oxidation-reduction potential of hydrolyzed chlorine will be high and that of chloramines (products of chlorine and ammonia) will be somewhat lower and generally lower still with organic chloramine formation (product of chlorine and complex, nitrogen-containing amino acid and protein compounds), Laubusch (1958b).

The innumerable side-reactions that may occur in sewage will not all progress at the same rate. Unless a sewage is well buffered, as mentioned previously, the addition of chlorine gas solution water may decrease the pH which in turn will increase the oxidation-reduction potential, or in other words encourage more and faster side-reactions. The opposite is true for the hypochlorites, which may explain the greater chemical reactivity of chlorine gas solution as compared to an equivalent strength of hypochlorite solution, Laubusch (1960c).

Increasing the sewage temperatures will also increase the reactivity of both free and combined chlorine, AWWA (1951). More chlorine (mass action) introduced initially will also increase the rate and completeness of oxidation reactions, Phelps (1957). Oxidizability of the organics and inorganics in sewage will likewise invite reactivity with chlorine. Many of these so-called side-reactions also represent direct bactericidal action or the products formed are bactericides. The chloramines are an example of a side-reaction forming a product still capable of bactericidal action.

The loss of chlorine in sewage by chemical side-reactions which consume Cl_2, $HOCl$, and OCl^- can be high. The addition of chlorine to sewage will for example reduce alkalinity by from 0.7 mg/l to 1.4 mg/l per each mg/l of chlorine applied. Dissolved sewage gases, such as H_2S, may enter into reaction with chlorine oxidants, Laubusch (1958b).

The reactions of chlorine with organic compounds are more complex. These reactions are known to involve addition, substitution, and oxidation of the organics by chlorine, Laubusch (1958c). These reactions in sewage are generally slow, as for example in the chlorination of ethylene. Ethylene, having a double bond, is easily oxidized at the double bond in aqueous solution, Sawyer (1960).



$$\mathrm{H{-}\overset{H}{\underset{}{C}}{=}\overset{H}{\underset{}{C}}{-}H} + \mathrm{Cl_2} \longrightarrow \mathrm{H{-}\underset{Cl}{\overset{H}{C}}{-}\underset{Cl}{\overset{H}{C}}{-}H}$$

It is well known in industrial waste treatment, especially with respect to slaughterhouse wastes that chlorination will precipitate proteins and fats, WPCF (1961). Organics containing nitrogen (proteins and amino acids) will react with chlorine to form chloro-derivatives. Some reactions will reduce part of the chlorine to the chloride, and some chlorine will combine with the organic and still retain some of its oxidizing and bactericidal potential.

Chloramine Formation

Thus far it has been pointed out that there is rarely any existence of HOCl and OCl^- in sewage, since a good portion of the chlorine applied will react with nitrogen compounds. Ammonia readily reacts with chlorine whether it be said that there is a strong affinity of chlorine for nitrogen or that chlorine readily replaces hydrogen. The product of hypochlorous acid and ammonia is called a chloramine, which still retains a little of the oxidizing power of HOCl, Moore (1951).

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

The product NH_2Cl, is called a monochloramine, and between a pH of 6.5 and 11 the reaction is quite rapid. The kinetic expression for the reaction rate is:

$$-\frac{dc}{dt} = (k_r)\ (C)(N)$$

$$k_r = 5x10^6$$

$-\frac{dc}{dt}$ = instantaneous rate of reaction, mols of HOCl or NH_3 per minute

C = concentration of chlorine, mols per liter

N = concentration of ammonia N. mols per liter

Tests have shown that the maximum rate of monochloramine production occurs at a pH 8.3. At 25°C a water receiving 0.8 mg/l of chlorine and 0.32 mg/l of ammonia nitrogen will convert 99% of the chlorine to the monochloramine in 1 minute at pH 8.3, in 210 minutes at pH 5.0 and 90 minutes at pH 11.0. The reaction also increases by a factor of 2.0 to 2.5 for every 10°C increase in temperature (Ibid.).

The monochloramine will dissociate into the dichloramine.

$$2NH_2Cl + H^+ \rightleftharpoons NH_4^+ + NHCl_2$$

The dissociation constant for this reaction is stated as follows:

$$\frac{(NH^+_4)(NHCl_2)}{(H^+)(NH_2Cl)^2} = Keq$$

Keq is 6.7×10^5 at a temperature of 25°C. At a ratio of total chlorine to ammonia nitrogen of 5 to 1, the following dissociation products are formed (Ibid.):

% Chlorine Present As:

pH	monochloramine	dichloramine
5	16	84
6	38	62
7	65	35
8	85	15
9	94	6

Figure 9 illustrates the rates at which chlorine components are formed.

The relative concentration of ammonia nitrogen and chlorine determine to some extent what chloramines are found. Additional HOCl reacted with a monochloramine will result in additional dichloramine formation.

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$$

More HOCl will result in formation of nitrogen trichloride.

$$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$$

The addition of even more HOCl will oxidize the nitrogen trichloride to gaseous nitrogen and hydrochloric acid. Nitrogen trichloride is also a dissociation product of the chloramines and will begin to appear at pH 4.4 and predominates at the very low pH range.

Breakpoint Chlorination

Breakpoint chlorination, commonly practiced for water chlorination, is rarely practiced in sewage chlorination. A discussion of this phenomenon is important to convey a better understanding of the chlorine

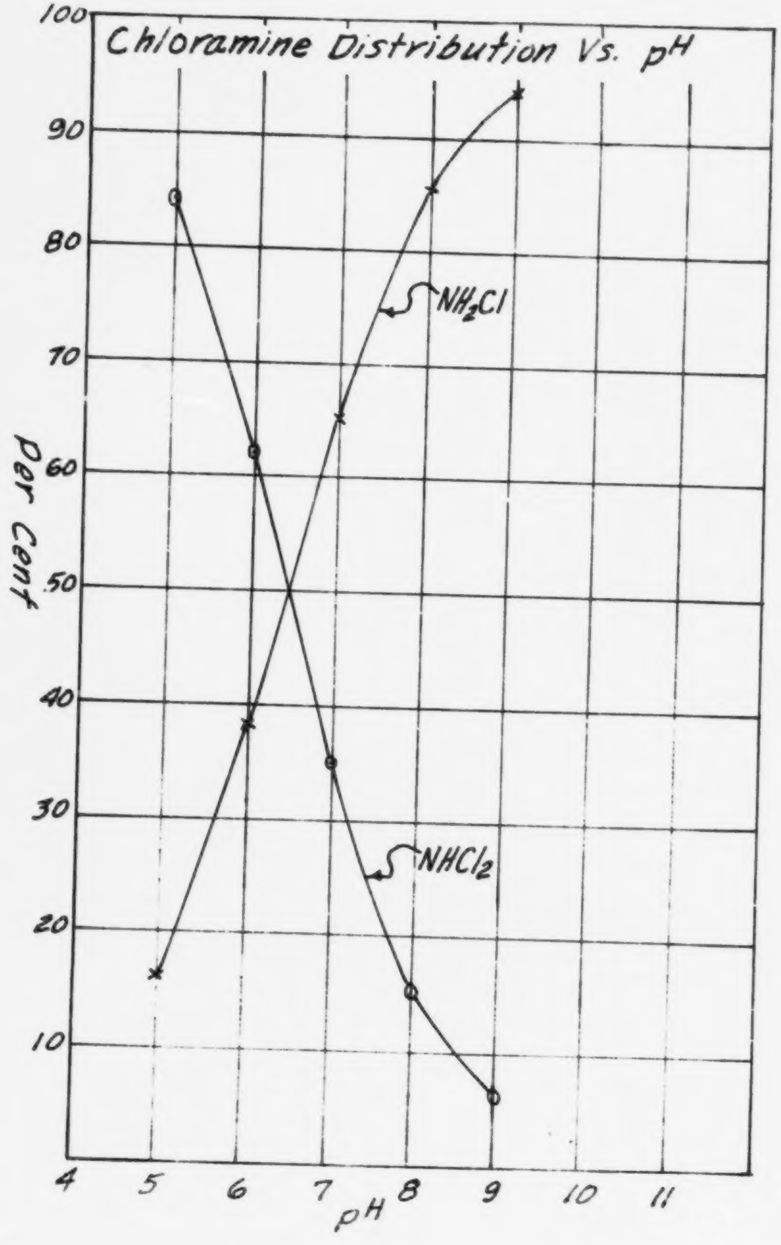
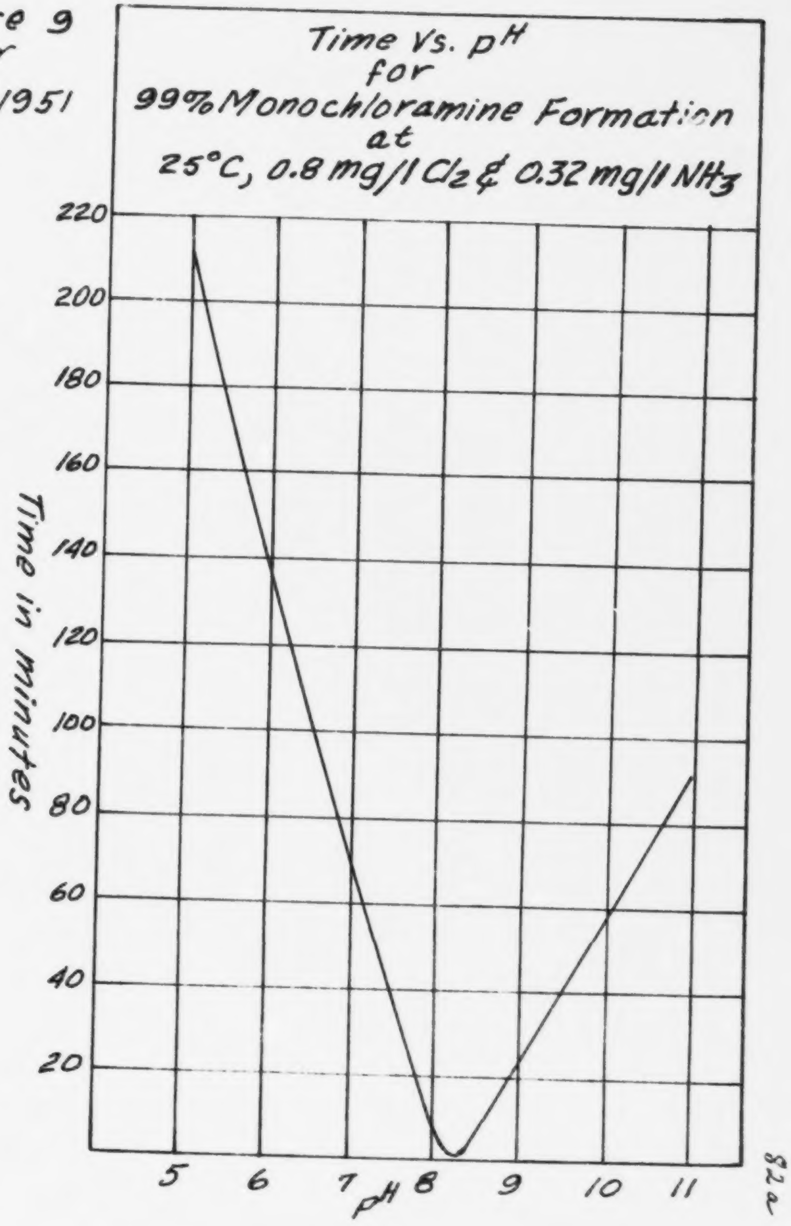


Figure 9
after
Moore, 1951

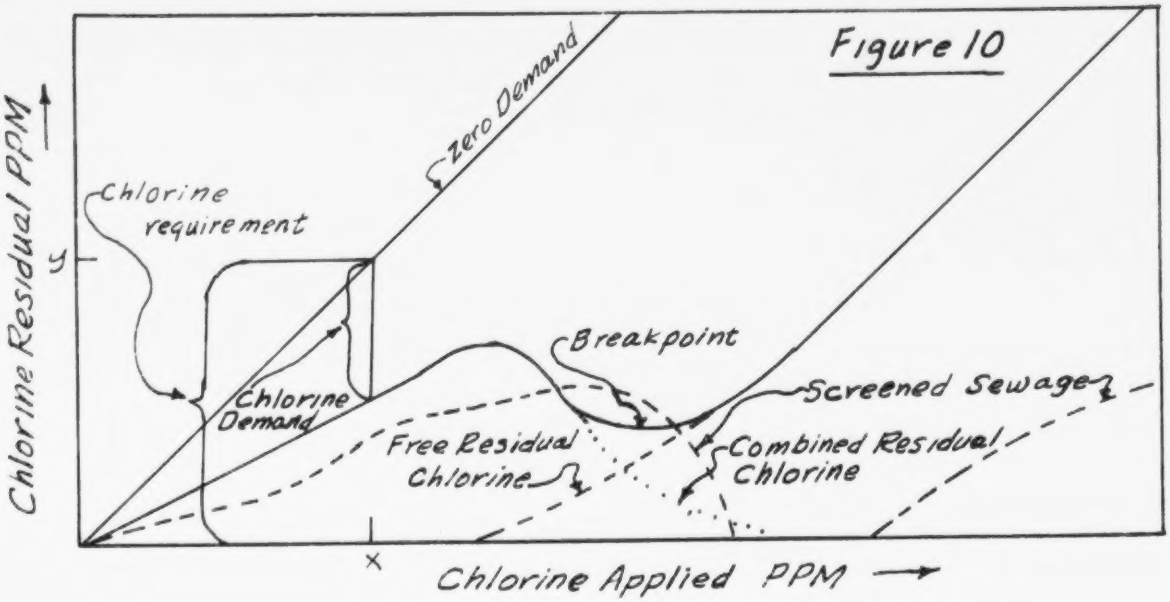


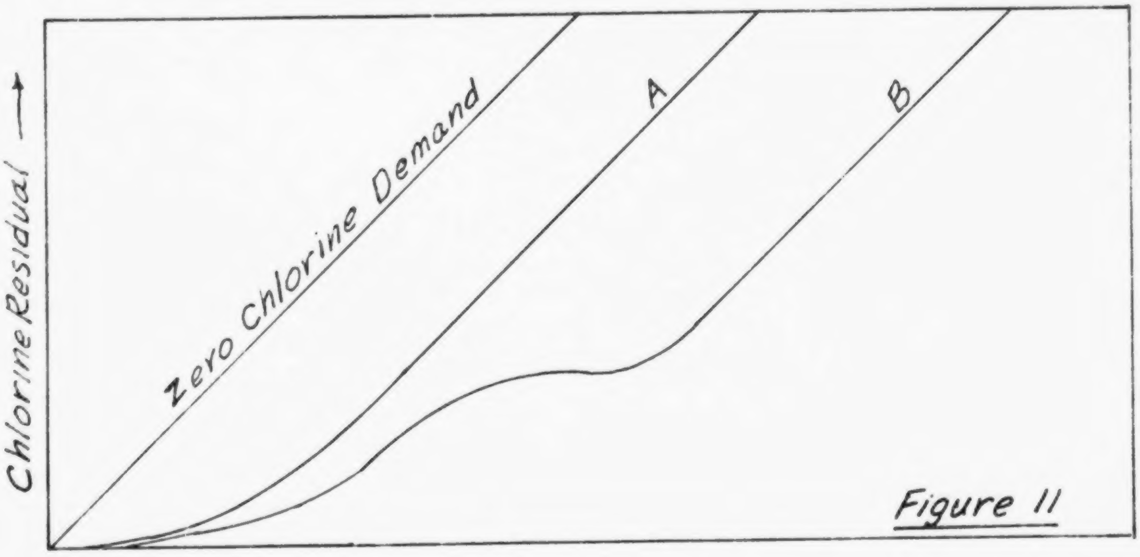
requirement or demand at dosages customarily applied as well as at the high dosage (super chlorination).

The breakpoint curve for a water or sewage is a measure of the chlorine residual resulting from a particular chlorine dosage as might be depicted in Figure 10. If all the chlorine that was applied showed up as a residual, the curve would ideally fall along the line of zero demand. Chlorine demand of water is represented as being the difference between the amount of chlorine applied and the amount of residual remaining at the end of a specific contact period, APHA (1962). The term "chlorine demand," when referring to sewage chlorination, is replaced by "chlorine requirement," a somewhat different term which describes the dosage required to achieve a particular residual after a particular contact time.

When chlorine is initially added to a water or sewage, some of it is inactivated such that it does not react to the residual test. Consequently, the breakpoint curve never achieves the line of zero demand, but due to side-reactions will deviate from it in characteristic curves dependent upon what compounds are involved in the side-reactions. Some compounds (for example, ammonia) even after reaction with chlorine will retain some oxidizing power and their chloro-derivatives (chloramines) will indicate a chlorine residual (combined residual). Increased dosage of chlorine will oxidize these compounds and after a certain dosage the chlorine residual will drop off. After these compounds have been completely oxidized the chlorine added will then appear in the residual as a free chlorine ($HOCl$ and OCl^-). At a dosage where the "free residual"

Breakpoint Chlorination Curves





After Griffin & Chamberlin (1941, 1945)

begins to appear and the "combined residual" begins to drop off, there is a hump or high point of residual followed by a valley or dip. The latter characteristic is termed the breakpoint. The breakpoint is important in water treatment because at that easily defined point it is known that the bulk of odor and taste-causing compounds have been oxidized. At dosages beyond the breakpoint dosage, there is essentially no more oxidation done by the chlorine, and the chlorine remains as OCl^- and HOCl and will parallel the line of zero demand.

Griffin and Chamberlin (1941, 1945) have made extensive studies of breakpoint chlorination of different types of sewage. The curve depicted on Figure 10 would be typical of a water containing just free ammonia or free ammonia with some nitrogen combined in other forms. The magnitudes of the hump and of the dip (breakpoint) of the curve will of course increase with respect to the degree of pollution.

The chlorination of water containing amino acids will follow the typical breakpoint curve for water containing ammonia, Feuss (1963). However, not all water will result in this characteristic curve. Figure 11 indicates by curve A the breakpoint curve that would result from chlorination of a clear, colorless, organic-free water also free of all forms of ammonia, algae, and other chlorine-absorbing materials. The breakpoint of this water is not sharply defined. Note that there will still be some chlorine that will be lost and it will not show as a residual. Curve B would represent chlorination of a water high in albuminoid ammonia or suspended organic matter. Here too the breakpoint is not clear and the hump and dip combine to form a plateau.

Of the several types of sewage chlorinated in the studies of Griffin and Chamberlin (1945) screened sewage demonstrated a somewhat flatter curve than that of water containing ammonia (Figure 10). The breakpoint does occur in the sewage and as the curve extends beyond the breakpoint it drops away from the line of zero demand. Both increased dosage and retention time accellerate this departure. This might be explained as slow chlorine reaction with the suspended solids in the raw sewage.

Primary settled sewage, having less suspended solids than the raw sewage demonstrated even less of a hump (75 PPM residual after 30 minutes with a 200 PPM dosage) and the breakpoint was evident at a 250 PPM dosage. The curve also had a tendency to fall away from the line of zero demand with greater detention time.

Chlorination of a 95% plain aerated sewage and 5% activated sludge mixture indicated even less of a pronounced hump and dip than the previous sewage mentioned because this sewage contained less organic material and ammonia than the raw and settled sewages. A gradual reduction of the residual with time also occurs under these conditions.

Chlorination of an activated sludge effluent, containing even less suspended solids and ammonia had a hump and dip that was barely evident. The curve was typical of water containing more albuminoid ammonia than free ammonia. Tests on the effect of chlorine on albuminoid nitrogen concluded that it is essentially unaffected by chlorine up to a dosage of 400 PPM and the breakpoint occurs due to an ability to destroy ammonia.

"The actual products of the breakpoint reaction and their mechanics are yet to be clearly defined," Feuss (1963). Ammonia oxidation and chlorine reduction occur when the molar ratio of chlorine to ammonia is greater than one and ammonia is completely oxidized at molar ratios of chlorine to ammonia of 2 to 1 provided there is enough time to complete the reaction, Fair and Geyer (1959). In practice the weight ratio of chlorine to ammonia required to remove the ammonia is about 15 to 1 and at times 25 to 1, Griffin and Chamberlin (1941). Before the breakpoint is reached, free chlorine will begin to appear and at the breakpoint the chloramines and free chlorine concentrations are about equal, Phelps (1957).

pH affects the breakpoint of sewage and water chlorination. Actual plant practice has shown that the optimum pH range for the ammonia-chlorine reaction is between 6.5 and 8.5, Griffin and Chamberlin (1941).

Another important point is that the longer the detention or contact time the lower the residual or the higher the chlorine requirement, Phelps (1957). The reactions of chlorine are not all instantaneous but are often a function of time.

Conclusions based upon the studies of Griffin and Chamberlin (1945) are summarized as follows:

1. "Typical breakpoint chlorine residual curves are produced when sufficient chlorine is added to sewage.
2. The 'hump' area of chlorine residual curves for sewage are somewhat lower than in water particularly on the ascending side of the hump.
3. Ammonia is destroyed progressively from the first appearance of a chlorine residual until the 'break' is reached where it completely disappears.

4. The ratio of chlorine to ammonia at the breakpoint in sewage appears to be in the same order as that found in water works practice, i.e., 10:1.

5. Albuminoid nitrogen is not appreciably affected by the amounts of chlorine used in the work, i.e., up to 400 PPM.

6. All appreciable BOD reductions take place ahead of the breakpoint. There is no evidence of increased application of chlorine adversely affecting BOD removal.

7. The greatest BOD reduction per pound of chlorine applied, in sewage of all strengths, occurs at the first appearance of a chlorine residual.

8. The greatest BOD reduction per pound of chlorine applied, up to the first appearance of a chlorine residual, occurs in the strongest sewages.

9. The greatest BOD reduction in percent, up to the first appearance of a chlorine residual, occurs in the most highly purified sewages.

10. The greatest overall BOD reduction in pounds of chlorine applied and in percent occurs in the most highly purified sewages.

11. Up to approximately 80% removals can be expected by chlorination of highly purified sewages."(BOD)

Variations in Sewage

The chlorine requirement of sewage is a function of several factors. A septic sewage is generally a high consumer of chlorine. Industrial and commercial wastes containing high volumes of reduced materials such as sodium thiosulfate, sulfur-containing detergents, cyanides, phenols, sulfur compounds, dyes, and like reducing agents will react with high volumes of chlorine, Keefer (1940). Sewage may pick up unusually high quantities of chlorine consuming agents under abnormal situations such as during the flushing out of sewers by high flows or from cleaning procedures.

The concentration of certain known chlorine consuming constituents in sewage will indicate the approximate chlorine requirement. A typical chemical analysis of a sanitary sewage may result in the concentrations shown in Table 13, Babbitt and Baumann (1958).

TABLE 13

CONSTITUENTS OF A TYPICAL SANITARY SEWAGE IN mg/l THAT MAY BE OF SIGNIFICANCE FOR CHLORINE REQUIREMENT

(After Babbitt and Baumann, 1958)

Constituents	Strong	Meidium	Weak
Solids (total)	1000	500	200
Suspended (total)	500	300	100
Dissolved (total)	500	200	100
Settleable (ml/l)	12	8	4
Biochemical Oxygen Demand (5 day, 20°C)	300	200	100
Oxygen Consumed	150	75	30
Nitrogen (total)	85	50	25
Organic	35	20	10
Free ammonia	50	30	15
Nitrates (RNO_2)	0.10	0.05	0
Nitrates (RNO_3)	0.40	0.20	0.10
Alkalinity ($CaCO_3$)	200	100	50
Fats	40	20	0

Generally the suspended solids make up most of the unstable organic substances in sewage. Nitrogeneous matter and carbohydrates will be the primary organics, with fats being only a small percent.

A close relationship exists between chlorine demand or requirement and the oxygen demand. The effect of age as well as temperature on a sewage demand is shown in the next table, Keefer (1940).

TABLE 14

Age of Sewage Hours	Chlorine Demand, PPM 20°C	 37°C
0	5.75	5.75
2	5.75	5.75
8	6.53	7.24
23	7.24	7.87

The above Table 14 indicates that with higher temperatures an aged sewage will develop an increased chlorine demand.

Raw and treated sewage will exhibit an hourly and even seasonal variation in chlorine requirement. This variation is of particular concern at plants employing primary treatment and those employing prechlorination. The lowest requirement within a day may be expected to occur during the early morning hours and the highest before noon and the afternoon. The domestic sewage at Buffalo, New York, for example, averaged a chlorine demand from 0.00467 to 0.0050 pounds per capita per day, but which varied within the day from 30% to 560% of the average for the particular day (Ibid.).

Salt water infiltration in sewers will also affect the chlorine requirement when such waters high in sulfates are reduced by septic conditions and the sulfides produced exert a demand, VanKleeck (1956b). Digester supernatant pumped back to the treatment system increases the chlorine requirement. This temporary load on the system could be excessive during certain periods of the day, and should be administered during times of lower loading. This is also true for sludge elutriates, vacuum filter filtrates, or any such substance that may introduce to the treatment an excessively high chlorine demand. Septic tank and cesspool pumpings are dumped at many sewage treatment plants. This can cause a serious problem at small plants (primary in particular). The operator must be aware of this additional load and know what chlorine dosage is necessary to cover the increased demand. Operators at some small plants feel that they cannot cope with this problem.

The degree of treatment afforded the sewage will, of course, affect the chlorine requirement as shown in Table 15 according to VanKleeck (1956b).

TABLE 15

Treatment	Chlorine Demand, PPM
Raw sewage	5-40
Primary tank effluents	5-40
Chemically-precipitated effluents	4-12
Trickling filter effluents	3-10
Activated sludge effluents	2-8
Sand filter effluents	1-5

It is noted that there is not much difference between raw and primary treated sewage and between trickling filter and chemically-precipitated sewage. Activated sludge effluents are markedly different from the first four treatments and sand filter effluents even more so.

SEWAGE TREATMENT PLANT APPLICATIONS

General

Although chlorination of sewage is intended primarily to "disinfect," the chemical character of chlorine causes it to be used for numerous other purposes. Some of these are biochemical oxygen demand reduction, odor control, insect control, grease control and as a coagulation aid. The types of chlorination as related to the point of application are upsewer, in plant, split, pre and post and are described in this section.

Upsewer Application

The term "upsewer" chlorination, as it implies, refers to chlorination of the raw sewage in the sewer prior to its arrival at the plant. Under some conditions, often with sewers of flat grades and insufficient scouring velocities, obnoxious odors develop from septic doncitions and create a nuisance condition. Sewer odors are often attributed to a sulfur reducing bacteria, Spirovibrio desulfuricans, which produces hydrogen sulfide gas, Grune (1955). Upsewer chlorination for odor control in the sewers will oxidize or neutralize the hydrogen sulfide as well as check the growth of the bacteria producing it. A less obvious effect of hydrogen sulfide is a persistant and often times expensive corrosion of concrete. The hydrogen sulfide takes oxygen from the air and is transformed to sulfurous and sulfuric acids which readily react with the concrete. To avoid the effects of hydrogen sulfide, chlorinators or hypochlorinators may be set up in pumping stations, along trunk sewers or interceptors to provide 3 to 15 mg/l of chlorine for reduction of each mg/l of hydrogen sulfide, Chamberlin (1948). Upsewer chlorination may also be employed to neutralize certain industrial wastes, lower bacteria concentrations before sewage treatment, and prevent sewage from becoming septic before its arrival at the plant.

Prechlorination

The term "prechlorination" refers to the chlorination of raw sewage at the treatment plant prior to any treatment such as sedimentation or the addition of flocculants. Primary treatment plants including those employing Imhoff tanks are amenable to prechlorination for several reasons:

1. The sedimentation tank or Imhoff tank can be used as a detention tank and with the long detention periods higher bacteria kills with lower chlorine residuals than "postchlorination" are possible. Prechlorination is preferred for primary treatment plants and can eliminate the need for postchlorination and the accompanying chlorine contact chamber, VanKleeck (1956b).

2. Better sedimentation of finely divided solids is achieved with prechlorination, Keefer (1940). Sedimentation interferences from biological slimes, rising septic sludge and some industrial wastes may be checked with prechlorination dosages of 2 mg/l or more. The dosage required depends on the waste, Chamberlin (1948). Prechlorination dosages of as little as 2 to 5 mg/l can break up grease emulsions to form floating solids that can be skimmed off (op.cit.). Chemical precipitation may also be improved by prechlorination, WPCF (1961).

3. Odors may be reduced by seasonal or continuous prechlorination in dosages enough to meet 25 to 50% of the raw sewage chlorine demand. Septic action or hydrogen sulfide production that is noticeable may be checked by 3 to 15 mg/l prechlorination, Chamberlin (1948).

4. Excessive algae growth in sedimentation tanks and conduits may be reduced by prechlorination.

5. Problems of Imhoff tank foaming may be met with prechlorination dosages of from 3 to 15 mg/l (Ibid.).

6. High flow or high chlorine demand shock loads to the sewage plant (e.g., from some industrial wastes, return sludge, digester supernatants, or septic sewage) may be prechlorinated and the effect on the treatment plant "leveled-out" by retention in the primary sedimentation tank.

7. In the case of overloaded sewage plants or excessive loads on the receiving stream, 1 mg/l chlorination of raw or clarified sewage will reduce the 5-day BOD by about 2 mg/l (Ibid.).

In Plant Chlorination

The term "plant" chlorination refers to chlorination at some treatment process within the sewage plant. Flies, ponding, and odors, three problems at times encountered with trickling filters may often be rectified by chlorination of the filter influent. During certain periods of the year, the filter fly, *Psychoda alternata*, will multiply upon trickling filters, and become a nuisance. To control the filter flies chlorine may be added to the filter influent in the realm of from

3 to 10 mg/l as long as the problem exists (Ibid.). The chlorine may be applied during the night when sewage chlorine demand is probably lowest and a chlorine residual more easily achieved.

"Ponding" usually caused by the accumulation of biological slimes, algae, and solids may clog a trickling filter and prevent sewage from draining down through the media. The filter may be cleared by applications of chlorinated lime or calcium hypochlorite on the filter surface to the amount of 8 to 12 pounds of "available" chlorine per each 1000 square feet of surface or the trickling filter influent may be chlorinated to produce a residual of from 2 to 10 mg/l at the nozzles of the distributors, which may require up to 30 or 40 mg/l chlorine dosage (Ibid.). This treatment may have to be continuous for a week or until the ponding is alleviated.

Odor problems for trickling filters may be checked by chlorine dosage at the primary settling tank influent or effluent of from 2 to 6 mg/l and continued until the problem is alleviated (Ibid.).

Problems commonly associated with activated sludge treatment include sludge bulking in the secondary clarifier and clogging of air diffusers. Sludge bulking, or light sludge, is usually attributed to biological slimes. A corrective step is to chlorinate the return sludge at least 2 minutes before introduction to the aeration tank with from 2 to 24 pounds of chlorine per 100,000 gallons of sludge returned, which is continued for a week or so until the problem is alleviated (Ibid.). Aeration tank diffusers must be inspected and cleaned periodically. Chlorine added to air headers at the rate of about 3 to 4 pounds per hour for periods each of 2 to 3 hours over several days may extend the cleaning periods. Similarly chlorine gas discharged into aeration headers, termed "aero-chlorination" may solve a serious grease problem, with the addition of from, "2 to 10 parts per million of chlorine gas and 0.02 to 0.20 cubic feet of air per gallon of sewage, with a 3 to 20 minute aeration period" (Ibid.).

Problems associated with sludge digestion may be corrected by chlorination under some circumstances. Situations where digester supernatant returned for treatment has proved to be an excessive load on the treatment system may be solved by chlorinating the return supernatant with dosages from 20 to 80 mg/1, the preferred time being the early hours when plant loading from raw sewage is low. Sludge being prepared for digestion may be more readily thickened by retaining a minimal chlorine residual in the liquor above the sludge in the thickening tank (Ibid.). Foaming in the digester may also be checked by chlorination,

Postchlorination

"Postchlorination" refers to chlorination subsequent to all other treatment. It occurs in primary and secondary treatment plants after the final clarifier and before the chlorine contact tank or outfall pipe if it is used as a contact chamber. Postchlorination is considered the final step of sewage treatment and disinfection.

Split Chlorination

"Split" chlorination is the simultaneous application of pre- and postchlorination. The increasing popularity of split chlorination is based upon its multiple benefits such as odor reduction especially if the raw sewage is stale or septic, less fat and oil skimmings, improved sedimentation, may produce bacteria kill results equal to other chlorination schemes with benefits well worth the cost of any extra chlorine used.

The possible points of chlorine application in the sewage treatment plant may be numerous, of course, the point or points of application will depend upon the intended purpose of chlorination. The more common points of application are shown in the following Table 16.

TABLE 16

POINTS OF CHLORINATION

Treatment	Raw Sewage	Prior to Secondary Treatment	Prior to Final Clarifier	Prior to Contact Chamber	Digester Super-natant	Return Sludge
Primary	X	n.a.	n.a.	X	X	n.a.
Chemical Coagulation	X	n.a.	X	X	X	n.a.
Trickling Filter	X	X	X	X	X	n.a.
Activated Sludge	X	X	X	X	X	X

n.a. = not applicable

With the availability of portable chlorination units and hypochlorinators, it might not be necessary to incorporate chlorination facilities at each of the application points mentioned above. The availability and versatility of a chlorination system that may easily be directed to several points in the plant would no doubt be appreciated by the plant operator when needed. The sewage plant designer should at least consider provision for "split" chlorination facilities.

Multiple points of application may be achieved by employing remote injectors at each of the application sites, provided that the dry chlorine gas lines are not excessively long from the chlorinator to the injector. Another approach may be to direct the chlorine solution from an injector near the chlorinator to the point of application. Panel mounted distributors with plastic valves and fittings for up to 2 inch plastic pipes (rubber-lined valves and fittings for the larger-sized pipe) are available, Wallace and Tiernan #5.260. Each line to a point of application should be fitted with two valves and a flow meter between, the upstream valve used for shutoff and the downstream valve used for flow control (Ibid.). Inclusion of multiple-point application to a chlorination system will require careful consideration of additional friction losses in piping, chlorination capacity, and booster pump requirements. In some cases it may be feasible to employ separate chlorination systems at one or more application points which may also serve as stand-by.

CHLORINE RESIDUAL METHODOLOGY

Ortho-Tolidine Method

The ortho-tolidine chlorine residual determination method is the most common used in sewage treatment plants. The ease of performing the determination using permanent colorimetric standards creates much of this popularity. A number of interferences cause erroneous readings using this method on sewage effluents. The commercial colorimeters use a specified amount of ortho-tolidine reagent added to a prescribed volume of sewage and the color developed is compared to a permanent standard. The method is described in Standard Methods for the Examination of Water and Wastewater and by the manufactures of the colorimeters. A few things should be kept in mind in using this test:

1. The sample should be quickly warmed to 20°C after the ortho-tolidine is added to the sample in order to develop full color by causing completion of the chemical reaction. A cold sample will not develop full color and would thereby indicate a lower residual than actually exists.
2. Interferences from turbidity, color certain metal ions and other substances can cause an erroneous reading which would also be low.
3. The ortho-tolidine reagent should be kept in a dark cool place but not below 0°C and should not be exposed to rubber. The reagent can lose its effectiveness with age.

Amperometric Method

The operating principle of this method is that with the use of a special galvanic cell the presence of an oxidizing agent such as chlorine or iodine can be measured by the use of a microammeter. The cell produces a small direct current which is proportional to the free chlorine or iodine in the solution. This means that if the free chlorine or iodine residual is increased or decreased the current change is indicated by the moving of the microammeter needle.

In water where there is only free chlorine, the titrating agent 0.00564N phenylarsine oxide can be used to titrate direct to an end point with each ml of the reagent reducing one PPM of free chlorine. The normal titration finds the current indicated by the microammeter decreasing as the titrating reagent neutralizes the chlorine thus decreasing the current. At the point when all the free chlorine is reduced the microammeter no longer indicates a change in current but remains in a fixed position.

Free chlorine is rarely found in sewage but it is usually found in combined forms as mentioned in the section on "Breakpoint Chlorination." The normal amperometric titration does not measure combined forms of chlorine. A method termed back titration is employed to measure the total chlorine residual which is generally measured in sewage. In this operation an excess of phenylarsine oxide reagent is titrated into the sample. The p^H is adjusted to a range of 3.5 to 4.5. At this p^H iodine is freed by the chlorine compounds when added in the form of a potassium iodide solution and the free iodine reacts instantaneously with the phenylarsine oxide. The excess phenylarsine oxide is then titrated with a free iodine solution. The free iodine titrated is subtracted from the total phenylarsine oxide applied and the balance represents the residual chlorine. The back titration begins with the microammeter needle remaining steady until the excess reagent is neutralized. After this point has been reached free iodine will remain in the sample and produce a current that will cause the needle to deflect upward. The microammeter acts only to indicate the point of neutralization.

The amperometric titration is extremely accurate and is not affected by many of the interferences that plague the ortho-tolidine method. Color turbidity and temperature do not interfere. Standard Methods mentions that interference from nitrogen trichloride or chlorine dioxide impairs the accuracy of the test since they titrate partly as free chlorine. This presents no problem in sewage since the titration is for total chlorine. Standard Methods also mentions interferences from copper when it exists in heavy concentrations.

The description of the amperometric and other residual chlorine tests are described in Standard Methods. Commercial titrators are available that make the amperometric titration a relatively simple, rapid and accurate means of determining chlorine residual.

Comparison of Ortho-Tolidine and Amperometric

The results of the ortho-tolidine and amperometric residual readings on the same samples have shown by comparison that the amperometric indicates a higher residual than the ortho-tolidine. This is because the amperometric measures the total chlorine with less interference than the ortho-tolidine. The difference between the two readings increases with increased organic content in the sewage Laubusch (1959d). Through the experience of Field Research and Development at NEWHSL it has been found that as the residual increases the difference between the ortho-tolidine and amperometric increases up to a maximum difference of between 5 to 6 PPM as shown in Table 18 and also is referred to in Standard Methods. This has been found in some secondary treated effluents as well as primary and is dependent on the quality of the effluent. Generally, there will be less difference in the two residuals taken on secondary treated effluent than primary. The increased difference with increasing residual is shown in the following Table from Strandskov, et al (1949).

Table 17 presents a comparison of chlorine residuals in effluent as determined by OT and amperometric titration.

TABLE 17

CHLORINE RESIDUAL (PPM)

O.T.	AMPEROMETRIC	DIFFERENCE	O.T. / AMP. %
0.25	2.1	1.85	12
0.18	1.9	1.72	9.5
0.15	1.6	1.45	9.4
0.12	1.5	1.38	8.0
0.10	1.4	1.30	7.1
0.08	1.4	1.32	5.7
0.05	1.2	1.15	4.2

In connection with the above described pattern we find that since the difference between the two readings tends to approach a maximum value as the residuals increase the percentage ratio of ortho-tolidine reading to amperometric reading increases.

CHLORINE RESIDUAL METHODOLOGY

Sewage effluent studies done by NFMESL using the actual conditions existing at the sewage treatment plants have shown that an ortho-tolidine residual is necessary in order to be certain of a high degree of coliform organism reduction. Tables 18 and 19 illustrate this point at a trickling filter plant and a primary plant. Good disinfection can be achieved without an ortho-tolidine residual provided the contact time is sufficient. Tables 18 and 19 show the variation in contact times that were encountered. Whenever a high coliform count was found it was accompanied by a short contact time.

Table 18 shows that at any amperometric residual of greater than 7.5 PPM under the conditions existing during the gathering of the data one could expect less than 100 MPN total coliform in the effluent. In order to be certain of this using the ortho-tolidine method a 5.0 residual would be necessary. To satisfy this requirement for ortho-tolidine the amperometric would have to be 9.0 PPM. The same data shows how the required residual can be much more closely regulated using the amperometric method.

It must be emphasized that in most plants there is difficulty in adjusting for varying contact times. Using, as a target, the residual needed for the shortest contact time encountered and the amperometric titration a satisfactory quality effluent could be assured. This would be true if the target MPN were 100, 1,000, 10,000 or whatever value is designated.

Day, Robert V. (1953) presents an evaluation of amperometric versus ortho-tolidine residuals under controlled conditions. He also presents a statistical analysis showing the importance of selecting the correct residual and contact time to provide the desired disinfection.

TABLE 18

TRICKLING FILTER PLANT EFFLUENT

Chlorine Residual Ranges (PPM)		Estimated Average Contact Time	Remaining Total Coliform Range
Amperometric	Ortho-Tolidine	(Minutes)	(MPN)
2.0-3.95	0.5-1.0	34-37	>2,400-93,000
3.0-3.45	0.35-1.4	31-37	460->2,400
3.5-3.95	1.0-2.0	34-46	43-11,000
4.0-4.45	1.0-2.0	31-46	43->24,000
4.5-4.95	1.4-2.5	25-59	23-11,000
5.0-5.45	2.0-2.5	23-59	9.1->24,000
5.5-5.95	2.0-2.5	31-42	23-1,100
6.0-6.45	1.5-4.0	24-42	3.6-11,000
6.5-6.95	2.2-5.0	24-42	15-430
7.0-7.45	2.5-5.0	23-42	3.6-11,000
7.5-7.95	2.5-4.0	29-42	3.6-23
8.0-8.45	2.0-5.0	23-?	23-93
8.5-8.95	2.5-5.0	37-42	9.1-23
9.0-10.45	5.0-7.5	37-59	9.1-93

TABLE 19

PRIMARY TREATMENT PLANT EFFLUENT

Chlorine Residual Ranges (PPM)		Estimated Contact Time	Total Coliform Range
Amperometric	Ortho-Tolidine	(Minutes)	(MPN)
0.0-0.5	0	37-55	230,000-9,300,000
1.05-1.5	0	38-50	93-930,000
1.55-2.0	0	39-61	23-23,000
2.05-2.5	0	48-61	23-4,600
2.55-3.0	0	41-48	23-1,500
3.05-3.5	0	39-60	3.6-4,600
3.55-4.0	0-0.4	40-59	<3->24,000
4.05-4.5	0-0.6	38-63	<3-1,100
4.55-5.5	0.4-1.2	41-53	7.2-460
5.05-5.5	1.0-1.5	36-49	9.1-1,500
5.55-6.5	1.0-1.8	43-53	3.6-23
6.55-7.0	2.0-2.5	37-43	<3-460
7.05-8.0	3.0-4.0	41-50	<3-15

RESIDUAL ANALYZERS, RECORDERS AND CONTROLLERS

The chlorine residual analyzers in use are the ortho-tolidine reagent and the amperometric types. Both types analyze a continuous sample pumped through a constant head device which provides constant flow. Special reagents are added and a reading is made in a sample cell fed by the constant head device. Both are adaptable to recording of the residuals and adjusting the feed rate to produce a specified residual. The desired residual must be determined by a sufficient number of bacteriological analyses of the chlorinated effluent that fall within the requirements of the receiving waters. Both types of analyzers can be connected to alarm systems to warn of failure to maintain the necessary residual.

Both the ortho-tolidine and amperometric analyzer apparatus require a certain amount of attention. Orifices tend to plug with particulate matter found in sewage effluents. The photosensitivity of the ortho-tolidine analyzer can be affected by discoloration and films forming on the sample cell. An automatic analyzer should be designed to fail safe, i.e., should anything interfere with the analyzing apparatus such as orifices being plugged, reagents being depleted or weakened so that residual readings are not being made the chlorine feed will not be discontinued.

Ortho-Tolidine

The ortho-tolidine residual analyzer requires a clear sample that does not have changes in color, turbidity, or matter in the sample that create various chlorine compounds that interfere with the analysis.

Actually this type of analyzer is best suited for water where the above mentioned interferences are not a problem. The experience of Field Research and Development, NEWHSL have been that it is difficult to adjust a photoelectric color intensity reading apparatus to a value that will be repeated when turbidity and color changes occur and in sewage these changes do occur.

The ortho-tolidine analyzer performs on the same principle as the color comparison kit but is read automatically by a photoelectric color intensity meter. The sample is allowed sufficient time to develop color.

Amperometric

The amperometric analyzer uses the principles of the regular amperometric titration and reads the sample residual chlorine and records it automatically. This analyzer is excellent for use with sewage since color, turbidity, and other interferences that exist in sewage that alter the ortho-tolidine reading do not interfere with it. Changes in the sample temperature must be accounted for by a manual adjustment or an automatic device. The reagents used in the analyzer recorder differ from those used in the standard amperometric titration described previously but produce the same residual reading. The analyzer is calibrated against the standard amperometric titration.

Compound Loop Control

The compound loop chlorination control system is an amperometric analyzer, recorder and chlorine feed rate adjusting operation. The feed rate is adjusted by readings obtained from two variables. One is the rate of sewage flow and as the flow increases or decreases the rate of chlorine feed is increased or decreased respectively. The other variable is the chlorine residual reading which also requires adjusting of the chlorine feed rate when it is above or below a predetermined residual setting. The operational problems are much the same as with just the analyzer recorder alone, with feed rate adjustment being the only additional operation.

There are a number of points that must be stressed to insure satisfactory performance.

1. There must be sufficient chlorine capacity.
2. The sampling point for the analyzer must be located so that it will produce a satisfactory residual at the outfall under all conditions.
3. The results of chlorination must be checked for periods of out of the ordinary flows or sewage quality, e.g., digester supernatant liquor withdrawal and maximum flows.
4. The sewage treatment plant personnel must be thoroughly familiar with the operation and maintenance of the equipment. Be able to clean, calibrate and make minor repairs.
5. The sewage treatment plant personnel must understand the relationship of contact time, chlorine residual, and sewage quality.
6. The unit must be designed to fail safe and transmit an alarm at failure.
7. The feed regulation sampling point must be near the beginning of the contact period. Figure 12 gives a schematic diagram of the compound loop system.

Observations made by Field Research and Development have shown these units capable of responding to normal changes in flow and sewage

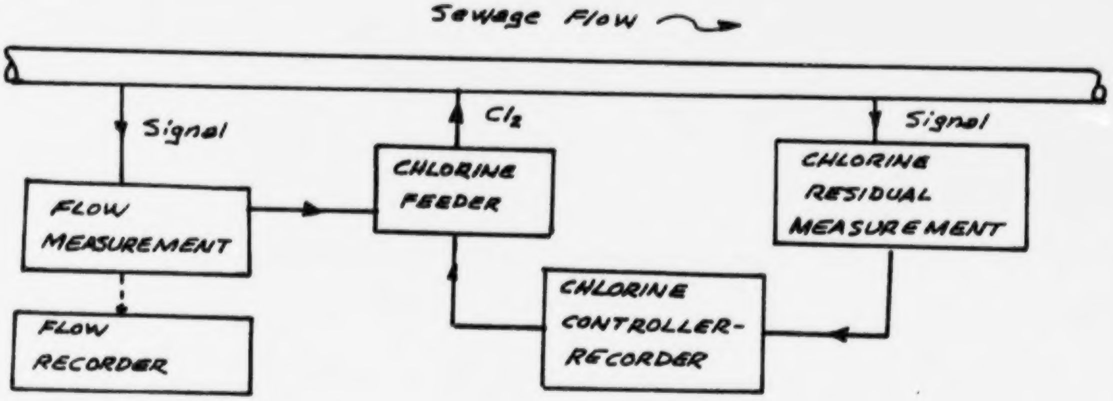

Sewage Flow
Signal
Cl2
Signal
FLOW MEASUREMENT
FLOW RECORDER
CHLORINE FEEDER
CHLORINE RESIDUAL MEASUREMENT
CHLORINE CONTROLLER-RECORDER

FIGURE 12

AUTOMATIC CONTROL OF
SEWAGE CHLORINATION

NEMHSL, FRD, S07 MAY, 1967

quality. The plant personnel must study each situation of substantial change and determine whether at these times the compound loop unit operation must be supplemented. Most of the increased requirement periods are predictable and controllable. The most difficult change to contend with is high flows that prevent satisfactory contact times. It was also observed that it is more difficult to obtain satisfactory performance from an installation in an old existing plant. For best results the unit should be designed into a new facility before being built or the old plant modified to whatever extent necessary for satisfactory performance.

Again, it must be stressed that when one of these units is put into operation a thorough study of the results under all varying conditions must be done before one can place full reliance on the unit.

Other methods of chlorine residual control are presented in "Chlorination Control," Laubusch (1959d) and some are described in the section of this paper, "Chlorine Feed Equipment," under "Measurement and Control of Feed."

PUBLIC HEALTH ASPECTS

Bactericidal Action of Chlorine

The many facets of this subject could be the subject of a lengthy paper in itself but the comments made here will be limited and general. The various forms of chlorine provide different rates of reaction for disinfection. Hypochlorous acid, HOCl, has been indicated as the best form of chlorine for disinfection. HOCl is not found in sewage disinfection because it readily reacts to form combined chlorine products. Therefore, in sewage disinfection we must depend on slower less effective agents. The section "Chemistry of Chlorination" particularly the topic, "Activity in Sewage" provides some detail on reactions of chlorine in sewage.

Regardless of the chlorine disinfecting agent involved, there are certain factors that determine bactericidal efficiency. The temperature, pH, organic compounds, and amonia all affect the efficiency. An increase in temperature will increase the disinfection achieved by the same amount of disinfectant at a lower temperature. Low pH increases the rate of kill and requires less chlorine to accomplish comparable disinfection than at higher pH values. Many organic compounds, especially the aminos in sewage react with chlorine to form combined chlorine compounds. Particulate substances can protect bacteria from destruction by shielding them from the disinfecting agent.

The importance of contact time and chlorine residual cannot be overemphasized. It is not necessarily the dosage of chlorine that is important but the residual remaining after a specified time. If all the chlorine is used up in reactions of oxidizing materials in the sewage so that none remains as a residual in combined form, then there is none for disinfection purposes.

According to VanKleeck (1956) the present theories on how chlorine destroys bacteria are as quoted:

1. "One or more bacterial enzymes are destroyed. Since enzymes are secreted by bacteria and are essential to their existence, one will not live without the other.
2. The chlorine penetrates the cell wall of bacteria, resulting in chemical changes in the cell protoplasm. Since protoplasm is a protein substance, death of the organism may well result from the formation of a poisonous compound or by actual coagulation of the protein in the cell."

The organisms that are of interested in the disinfection process were listed by Moore (1951).

1. Escherichia coli and the coliform group which are not classified as pathogens but are used as indicators of the presence of pathogens and are used as the basis for testing sanitary water quality.
2. The enteric bacteria such as Salmonella which cause typhoid and dysentery.
3. The intestinal protozoa of which one, endamoeba histolytica, causes amoebic dysentery.
4. Worms.
5. Viruses such as infectious hepatitis and ECHO virus.

As previously mentioned the efficiencies of disinfection of various chlorine forms differ. HOCl is more effective than OCl^- and all of the combined forms of chlorine. The relative efficiencies of the various forms also differs from organism to organism. Thus, the residual and contact time needed to inactivate or destroy one type of organism, say coliforms does not effect some other, e.g., infectious hepatitis virus. For some infectious agents the necessary chlorination requirements for disinfection have not been determined and the determination of these requirements may be critical to shellfish growing areas.

Effects of Chlorination on Estuarine Waters

The complex nature of an estuary makes it difficult to separate one factor from the others. In this instance we will present some findings and some possible problems on the single topic of coliform relationship to disinfection and discharge to estuaries. The hydrographic and meteorologic effects cannot be entirely ignored in the discussion but will not be stressed. There are very little data available on this subject but we will present what we have with plans to enlarge upon it as data become available.

A shellfish growing area study was done by NEMHSL during September 1965 (NERC, 1966). One of the results of the study was improved chlorination practice at the main source of bacterial contamination. Upon the first visit to the waste disposal units, chlorination was inadequate and the dose was increased to correct this deficiency. The bacteriological quality of the estuary downstream improved as the effluent quality improved during the time of this study.

The following Table 20 presents the results of improved chlorination and emphasizes the need for a residual after sufficient contact time. The total coliform values are for the 3 tube MPN test of the effluent sample after the chlorine contact tank of an activated sludge plant.

TABLE 20

Day of Study	Flow cfs.	Total Coliform MPN	Chlorine Residual (O.T.) (PPM)	Chlorine Dosage Gal./day
1	0.06	<30,000	-	-
2	0.08	46,000,000	0.00	-
3	0.16	<30,000	0.00	-
4	0.09	4,600	0.1	5
5	0.08	<3,600	0.35	7
6	0.12	360	0.75	8
7	0.08	<300	0.35	7
8	0.16	910	0.75	8
9	0.09	<300	0.1	60
11	0.23	110,000	Trace	8
11	0.11	73	1.4	10
11	0.12	<300	0.75	10
11	0.16	30	0.75	10
11	0.09	<30	2.0	10
11	0.09	73	0.5	10

Figure 13 shows the changes in bacterial quality of the estuarine water at the most frequently sampled point of the study. There is a strong indication that the decrease in coliforms in the estuary was related to improved disinfection at waste sources since, to the knowledge of the survey team, no other significant alterations of pollutant discharges occurred during the time of the study.

A problem that must be mentioned is the possibility of aftergrowth of indicator organisms after the chlorinated effluent is diluted in the receiving waters and the chlorine is no longer effective. This has been

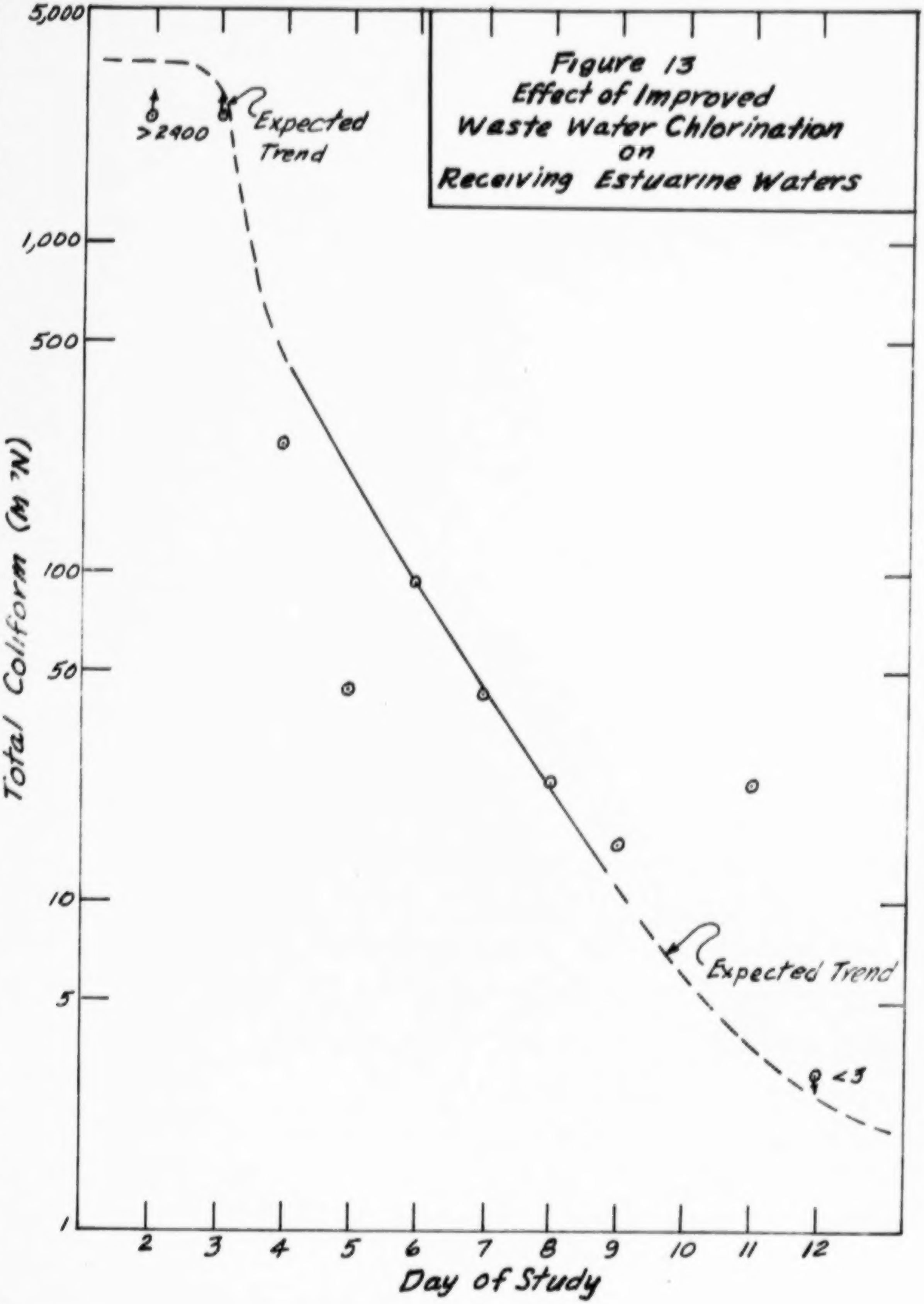


Figure 13
Effect of Improved
Waste Water Chlorination
on
Receiving Estuarine Waters

known to happen in fresh waters and has not been shown conclusively to be impossible in estuarine waters if conditions were favorable.

Chlorination Standards

Disinfection standards or requirements should be based on the resultant bacteriological quality of the treated water not on a dosage rate or residual of chlorine. To have chlorine residual standards to aim at is a practical easy way to achieve disinfection but in order for such standards to be effective they must be proven so in each plant they are used. The varying degree of treatment and quality of effluents demand that each be investigated individually to show that the standard being applied does meet requirements for bacteriological kill.

Laubusch (1958d) in his review of "State Practices in Sewage Disinfection" described interstate compacts of which only one had enforcement powers. This was the Ohio River Valley Sanitation Compact (ORSANCO) and their requirements were that discharges to the Ohio River have the coliform counts reduced by 85 percent May through October and at other times 65 percent. These requirements are to produce river waters having not more than 5,000 coliforms per 100 ml per month and not exceed the 5,000 in 20 percent of the samples for the month nor 20,000 per 100 ml in more than 5 percent of the samples, Day et al (1953). This type of standard is aimed at the end quality of the receiving waters and thus determines the disinfection necessary. To set a percent reduction required can be misleading and unsatisfactory in many instances. For example, if there are 1,000,000 coliforms per 100 ml in a nonchlorinated effluent and we reduce this by 99 percent we still have 10,000 coliform per 100 ml. Laubusch (1958d) points out that most states consider the effect of the wastes on the receiving waters and on uses of the waters in developing their standards.

Chlorination of wastes discharged into shellfish growing waters is more critical than for any other present public health reason because of contamination of a raw food product. Furfari (1967) has reviewed this problem and a copy of his findings on standards in coastal states along with his comments is included at this point, and are as follows in quotes:

"Laubusch (1958)[1] reviewed the chlorination standards of the states. From his summary, Tables 1 and 2 have been derived to show the practices of the coastal states. Although some of these values may have been changed since the report, the comments in the next paragraph for similar standards will still pertain.

Table 1

Chlorination Standards for Coastal States
(after Laubusch, 1958)

Chlorine Residual		Number of States
Trace		3
0.5 mg/1		3
1.0 mg/1		2
1.0-2.0 mg/1		1
	Subtotal	9
	Not Specified	13
	Total	22

(Note: one State, not above, has a coliform index for the effluent.)

Table 2

Contact Time Standards for Coastal States
(after Laubusch, 1958)

Time (minutes)	Number of States	Time (minutes)	Number of States
15 (peak hourly or max. pumping)	3	30 (Average flow)	4*
15 (Average flow)	1	10-15 (no specified flow)	1
15 (max. flow)	4*	15 (no specified flow)	1
20 (Average flow)	3	20 (no specified flow)	1
		Nothing Specified	6
		Total	24

*One state mentioned twice.

WEAKNESSES OF STANDARDS

The standards given in Tables 1 and 2 are deemed inappropriate and inadequate for the shellfish program for the following reasons:

1. The chlorine residuals are those of combined chlorine for most sewages, and as is known (and described later), combined chlorine is slow and even ineffective in killing bacteria and viruses especially.

2. For the contact times and the scope of the residuals given, the contact times are inadequate to totally inactivate the virus of infectious hepatitis and other viruses.

3. By not defining the performance that these residuals and times are expected to accomplish, in the effluent as well as in the waters of the harvest areas, an uncertain number of bacteria and enteric viruses are allowed in these two waters.

4. These standards were derived originally for coliform kill rates and the nearly parallel typhoid bacteria death rate. However, the major concern now is not typhoid fever but infectious hepatitis. In the future

it may be another pathogen. The prime consideration, therefore, revolves around the epidemiological significance of the sewage treatment efficiency. The prevalence of diseases in the community should play a role in the decision process.

5. These standards, apply evidently to all situations in a state, but are not specific enough for the shellfish program. Discharges to a fresh-water stream as compared to discharges to a shellfish harvest area will require two totally different types of standards.

6. Character of sewage does not take the place it should in the standards. BOD per se is of little importance to the shellfish program. BOD is of importance only as it may reduce effectiveness of the disinfection.

7. Laws such as these, that require chlorination to take place at the levels prescribed by law, are unenforceable because "fail-safe" equipment which insures uninterrupted chlorination have not been installed."

These weaknesses pointed out by Furfari (1967) led him to indicate that no general coliform or chlorine residual standards should be set for effluents discharged into shellfish growing waters but each situation should be regulated individually with respect to providing satisfactory water quality in the receiving waters.

Morris, J. Carrol (1966) indicated that considerable research should be done in order to more definitely determine the requirements of disinfection for viruses and other hardy pathogens under the varying conditions found in water before a standard that is certain of working can be set. This need is also important in the disinfection of sewage, especially where shellfish are within reach of contamination from sewage treatment plant effluents.

APPENDIX A

ELEMENTAL CHLORINE

The chlorine atom (atomic weight of 35.457), with an electronic configuration as shown in Figure A-1, has 2 electrons in its first ring, 8 in the second ring, and 7 in the third ring (one less electron in the third ring than that for an inert gas), Quagliano (1958).

This electron arrangement causes the atom to tend to fill its outer ring with one more electron. The atom can achieve this by sharing an electron with another chlorine atom. This covalent arrangement forms the chlorine molecule Cl_2 (molecular weight of 70.914) with the electronic configuration as in Figure A-2.

Chemically, chlorine closely resembles oxygen. The two elements will not combine directly with each other or with carbon, nitrogen, and the inert gases, Frey (1959). Chlorine will react readily where it can acquire an extra electron in its outer ring thereby assuming a valence of -1. This character of chlorine causes it to be termed a good oxidizing agent. Chlorine less commonly has been known to have valences of +1, +3, +5, and +7, Sorum (1955).

Like oxygen, chlorine can support the combustion of certain substances, such as finely divided forms of antimony, arsenic, busmith, copper, iron, phosphorous, boron and certain of their alloys, Laubusch (1963). Dry chlorine gas or liquid will react to some degree with aluminum, gold, mercury, selenium, tellurium, tin, and titanium usually forming binary ionic compounds. At high temperatures steel and most construction metals and their alloys will also react with chlorine, however, below 110°C (230°F) copper, iron, lead, nickel, platinum, silver, steel, tantalum, are resistant to chlorine.

Chlorine reacts with nonmetals usually to form covalent compounds, Hardie (1959).

Figure A-1
Chlorine Atom

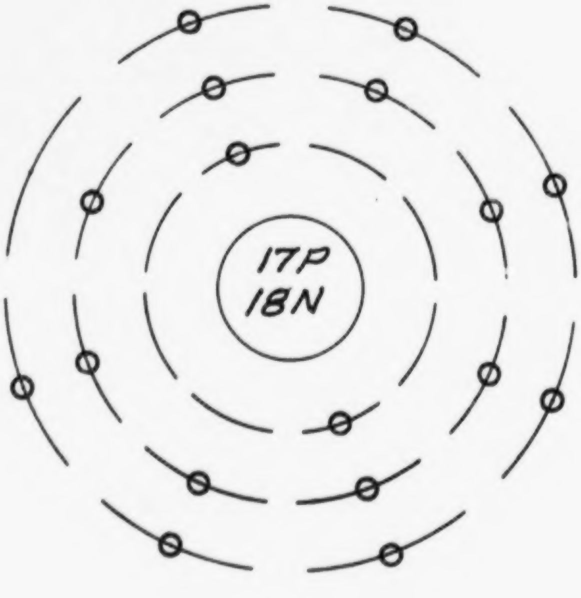
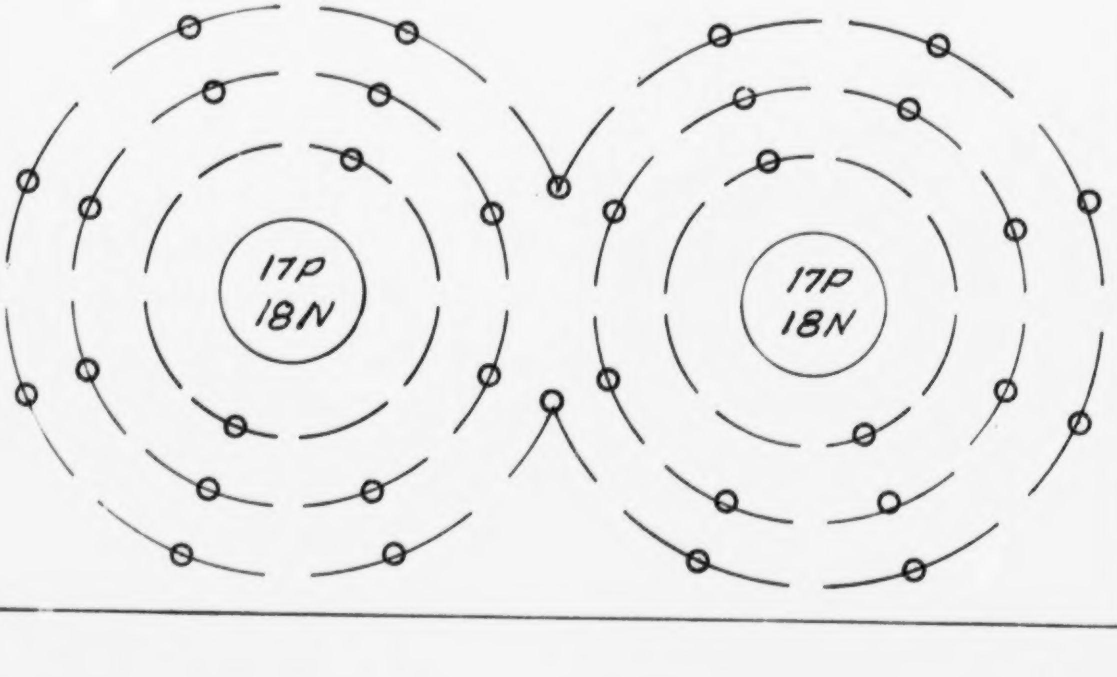


Figure A-2
Chlorine Molecule


17P
18N
17P
18N

APPENDIX B

MANUFACTURE OF CHLORINE

Electrolysis

Prior to the first production of chlorine by man, during the latter part of the 18th Century, it had been known only as a hot volcanic gas. The history of commercial chlorine production probably started with Cruikshank in 1800, when he charged a brine with electricity and evolved chlorine. It followed from the principles explained in 1834 by Faraday's Laws of Electrolysis, as stated below that (Shortley and Williams (1955):

1. The quantity of substances freed at the electrodes is in direct proportion to the quantity of electricity passing through the solution;

2. This quantity of electricity always releases the same number of gram equivalents of substances at the electrodes. The quantity of electricity that will release a gram equivalent is called a faraday which is equal to 96,494 coulombs (96,494 amps/sec.). For example, this will release 35.5 grams of chlorine at one electrode and an equivalent of another substance at the other such as 1.0 gram of hydrogen. The gram-equivalent weight of a substance is its molecular formula weight divided by the number of electrons required for the oxidation or reduction of the substance.

Commercial Production

The several varieties of electrolytic cells that are employed in commercial chlorine production can be classed basically as either the diaphragm-type cell or as the amalgam-type cell (mercury).

Most of the 68 chlorine producing plants (1 January 1964) in the United States employed the diaphragm-type cell. The name of this type cell is derived from the porous asbestos pads which separate the positive and negative electrodes for the purpose of allowing electrolyte movement without reaction of electrolysis products. The diaphragm-type cell receives a continuous flow of brine (electrolyte) which is charged with several thousands of amperes causing free chlorine to be liberated at the anode (positive electrode of an electrolytic cell) and hydrogen to be liberated at the cathode (negative electrode). Due to economic considerations electrolysis is not completed in the cell so that the cell waste effluent at best consists of caustic soda diluted in brine.

The amalgam-type or mercury cell, predominant in Europe and becoming increasingly popular in the United States, employs a somewhat more sophisticated scheme of electrolysis. As with the diaphragm cell, the brine flow is continuously pumped through the cell. The sodium which is liberated from the brine, forms an amalgam with the mercury cathode and is drained from the cell in this state to another electrolytic cell where it is purged of the sodium. The sodium is liberated from the amalgam by forming caustic soda with water contained in the second cell. The caustic soda is drained-off as a by-product instead of a waste as is the case for the diaphragm cell. The mercury thus cleansed of sodium is returned to the primary cell for reuse.

Impurities in Liquid Chlorine

In the past there have been occasional complaints from water and sewage plant operators that chlorinator lines and parts become clogged due to impurities in liquid chlorine. This situation is serious if it disrupts chlorination and is of particular concern at unattended treatment plants or at those having only one chlorinator. One New Jersey sewage plant operator interviewed, for example, reported to have received a chlorine shipment from a particular dealer which caused severe clogging problems. Convinced that poor quality chlorine caused this difficulty, he then purchased chlorine from another dealer and since has experienced no chlorinator difficulties. Another operator in Rhode Island opened his chlorinator full each morning to "blow out impurities." Whether or not changing chlorine dealers or blowing-out chlorinators is a cure to chlorinator clogging, it is not the solution. Chlorination has been disrupted and the damage has already been done. It is necessary to know what these impurities are and how to avoid the problems arising from them.

Returning to liquid chlorine prpduction, it is known that the hot chlorine gas drawn from the electrolytic cell contains water and other impurities. Hardie (1959) states that from 5 to 7% by volume of commercial chlorine gas may contain other gases (H_2, CO_2, N_2, O_2). The chlorine produced by amalgam-type cells may contain up to 0.5 to 1.5% hydrogen and from 0.25 to 0.50% carbon dioxide and the diaphragm cell produces a chlorine gas with much less hydrogen but up to 2% carbon dioxide.

The types of chlorine impurities can be quite diverse, Laubusch (1959a):

Gases
  Carbon Dioxide
  Hydrogen
  Oxygen
  Nitrogen

Nonvolatile Solids
  Ferric chloride*
  Ferric sulfate

Volatile Solids
  Hexachlorabenzene*
  Hexachlorethane

Volatile Liquids
  Bromine
  Carbon tetrachloride
  Carbonyl chloride
  Hydrochloric acid
  Methylene chloride
  Nitrosyl chloride
  Nitrogen tetroxide
  Nitrogen trichloride*
  Silicon tetrachloride*
  Sulfuric acid

---

*Known troublesome impurities

An example of commercial chlorine impurities has been given by Laubusch (1963):

"According to one manufacturer, the following may be taken as illustrative: Gaseous as Co_2, O_2 and N_2 (0.50%, 0.04% and 0.07% by volume, respectively); liquid, 40 mg/l total, largely carbon tetrachloride, chloroform and chloroethanes; solid, 25 mg/l total, largely hexachloroethane and ferric chloride."

Water and chlorine constitute a highly corrosive combination. For corrosion prevention during storage, the water is removed by scrubbing with sulfuric acid. As the chlorine gas is cooled and compressed to a liquid, it is further purified by blowing-off noncondensed gases. There are methods available to further refine liquid chlorine, however, their employment is an economic consideration. Laubusch (1959a) of the Chlorine Institute has stated the view of the chlorine producer:

"Chlorine producers do not aim to provide a product absolutely free of impurities; this is impractical on a commercial scale. Their aim is to supply a product which is reasonably free from those impurities whose presence in appreciable quantities is known to be unsafe or objectionable in transportation and use.

All chlorine producers market a chlorine of greater than 99.5 percent purity, and they ordinarily remove or reduce those particular impurities believed likely to create difficulties in transit and in process applications.

...chlorine containing as little as 0.2 percent of certain impurities may cause great trouble in a chlorinator."

Federal Specification BB-C-12C, Chlorine (U.S. Govt. Printing Office, March 21, 1955) and the AWWA Specification B 301-59 state:

"Chlorine shall be 99.5 percent pure by volume as obtained from vaporized liquid chlorine and suitable for use in chemical manufacture and sewage and water treatment," Laubusch (1963).

No one has done sufficient investigation to provide limits of allowable concentrations of impurities that will not be objectionable.

The production of "sanitary" chlorine represents only a small percentage of the total chlorine tonnage produced in this country and the voice of chlorine consumers using chlorine for water or waste treatment, regardless of any enthusiasm in its demands of the chlorine industry, is small.

It should be recognized that additional impurities may be introduced into commercial chlorine at any point between the manufacture and actual application. Since sewage plant operators customarily do not check the quality of newly purchased chlorine, their only protection is the reputation of the manufacturer's and dealer's products.

The problem of chlorine impurities has prompted a PHS-sponsored research project to evaluate and improve present chlorine qualitative analyses. Progress of this project, reported by DeVries and Savarier (1960) at Purdue University, shows the initial result as an improved laboratory test for silicon tetrachloride in chlorine. Further efforts will involve a chromatographic technique for chlorine analysis and a test to measure the nuisance causing impurities.

The situation thus far is summarized by Laubusch (1959a):

"It remains to be established whether the final solution to the impurities problem will lie in more rigid quality control, improved operation and maintenance procedures, modification of equipment, or a combination of all three factors."

APPENDIX C

ORIFICE EQUATION

The orifice plate is a simple device, easy to calibrate and once calibrated the pressure drop ΔP (as determined by a manometer) can be correlated to a flow, customarily indicated on chlorinator scales in pounds per day. The relationship between the pressure drop and flow rate is not linear, and unfortunately at low flows or when ΔP is small, the measuring units are close, and control is difficult since precision is poor. Another disadvantage of the orifice and manometer device is the possibility of the measuring fluid being blown or sucked out of the manometer by excessive pressures or vacuums developed in the conduit although manometers have been developed which would lessen chances of this occurring.

The orifice functions in the manner described by the following equation, George et al (1950):

$$W = CoAo\sqrt{\frac{2\,go\,\rho\,(\Delta P)}{1-(Ao^2/A_1{}^2)}}$$

W = mean rate of flow

Co = orifice coefficient

Ao = cross-sectional area of orifice opening

go = sea level acceleration of gravity

ρ = density of flowing material

ΔP = drop of pressure across orifice

A_1 = cross-sectional area of conduit

APPENDIX D

CHLORINE REQUIREMENT TEST

The object of the chlorine requirement test according to Standard Methods is a "practical and realistic approach to the control of disinfection of sewage and to the estimate of the chlorine required."

"In plant studies, the test should be run with the minimum and average contact times corresponding to different flow conditions, to determine the average and the variations from the average of the number of coliform organisms in the effluent.

In order to establish the chlorine requirement for a given coliform density in the effluent with suitable precision the test should be repeated at least ten times on different samples under each of the various conditions," APHA (1960).

The final step of the requirement test for laboratory studies involves the preparation of a standard chlorine solution prepared by passing chlorine gas through distilled water or tap water until it contains approximately 1.0 mg of chlorine per ml of volume. This solution will be unstable and it is suggested that it be made up fresh daily or frequently standardized by the Iodometric method using 5 ml of the chlorine water and 0.025N sodium thiosulfate. The chlorine content is then described by:

$$\text{mg/ml of } Cl_2 = \frac{(\text{ml of } 0.025N\ Na_2S_2O_3)(0.8864)}{5} = (\text{ml of } 0.025N\ Na_2S_2O_3)(0.1773)$$

To each of a series of 1 liter containers, place 500 mls of sewage. While stirring the samples gently add increasing quantities of the chlorine solution in suitable increments of sufficient range to include a dosage certain to produce the desired result. At the end of the stipulated contact times, the residual chlorine is measured on each portion.

To measure the degree of colicidal action of the dosage, it is necessary to add to each of the above sewage portions about 0.5 ml of sodium sulfite to halt the chlorine action. Each portion should then be tested for the MPN value. The sodium sulfite is prepared by weighing 10 grams of anhydrous Na_2SO_3 and diluting to 100 ml in distilled water and is heated to boiling. This solution should be prepared daily.

The precision of the chlorine requirement test is admittedly of a low order with only one sample results due primarily to the inaccuracy of the MPN test. The test too is not comparable from plant to plant or from time to time since each plant's sewage is different and it changes with time.

APPENDIX E

AWWA TEST FOR AVAILABLE CHLORINE

The test for solid form hypochlorites as paraphrased from the "AWWA Standard for Hypochlorites" is as follows:

1. Approximately 7 gms (weighed) of chlorinated lime or calcium hypochlorite is placed in a nonmetallic mortar, moistened with water, and finely ground.
2. The mortar is rinsed of its contents into a 1 liter flask and the volume brought up to 1 full liter with distilled water.
3. Twenty-five ml of the 1 liter solution is transferred to a 250 ml Erlenmeyer flask and to this is added about 1 gm of crystalline KI.
4. The solution in the Erlenmeyer flask is made acid by the addition of about 4 ml of glacial acetic acid.
5. This solution is then titrated with 0.1N sodium thiosulfate using starch as the indicator near the endpoint.

$$\%\ \text{avail. chlorine by weight} = \frac{(\text{ml } 0.1N \text{ sodium thiosulfate})(40)(0.003546)(100)}{(\text{weight of sample})}$$

This equation may be derived as follows:

$$\%\ \text{available chlorine by weight} = \frac{(\text{grams of available chlorine})\ (100\%)}{(\text{weight of sample in grams})}$$

Since grams-equivalents of the "available chlorine" (subscript 1) equal gram-equivalents of the sodium thiosulfate (subscript 2), or in terms of the milliliters and normalities (gram-equivalents per liter of solution):

$$(N_1)(ml_1) = (N_2)(ml_2)$$

$$N_1 = \frac{(N_2)(ml_2)}{(ml_1)}$$

$$= \frac{(0.1\ \text{gram-equivalents})(\text{ml } 0.1N\ \text{sodium thiosulfate})}{(\text{liter})(25)}$$

Note that 25 milliliters of the hypochlorite solution were titrated and not the full liter. Normality of the "available chlorine" can also be restated:

$$N_1 = \frac{(\text{grams of available chlorine})}{(35.46\ \text{grams/gram-equivalent weight})(\text{liter})}$$

Note that "available chlorine," though not necessarily a measure of chlorine itself, is stated in terms of chlorine (gram-equivalent weight = 35.46 grams). The two equations stated above expressing N_1 can be combined:

$$\frac{(0.1\ \text{gram-equivalent})(\text{ml } 0.1N\ \text{sodium thiosulfate})}{(\text{liter})(25)} = \frac{(\text{gram of available chlorine})}{(35.46\ \text{grams/gram-equivalent weight})(\text{liter})}$$

$$\text{grams of available chlorine} = \frac{(0.1)(\text{ml } 0.1N\ \text{sodium thiosulfate})(35.46\ \text{gram})}{(25)}$$

$$\%\ \text{avail. chlorine by wt.} = \left[\frac{(\text{ml } 0.1N\ \text{sodium thiosulfate})(40)(0.003546)}{(\text{weight of sample})}\right](100\%)$$

This equation can be further reduced:

$$\%\ \text{available chlorine by weight} = \frac{(14.184)(\text{ml } 0.1N\ \text{sodium thiosulfate})}{(\text{weight of sample})}$$

The weight of sample incidently is the 7± grams of hypochlorite finely ground in the mortar.

The procedure for measuring the "available chlorine" of sodium hypochlorite is as follows, AWWA (1953):

1. Twenty ml of the sample is accurately measured and placed in a 1 liter volumetric flask and distilled water is added to make a full liter.
2. Twenty-five ml of this solution is transferred to a 250 ml Erlenmeyer flask and to this is added approximately 1 gm of crystalline KI and 4 ml of glacial acetic acid.
3. This is titrated with 0.1N sodium thiosulfate using starch as an indicator near the end point.

Volume or trade % = (ml 0.1N sodium thiosulfate)(40)(50)(0.003546)(0.1)

This equation may be derived as follows:

Since a 1% solution will have a concentration of 10,000 mg/l or 10 gm/l then the following equation may be formulated for any percent solution:

$$\text{Volume percent} = \left(\frac{\text{gram of available chlorine per liter}}{10}\right)$$

In the procedure, 20 ml of the hypochlorite sample has been diluted to 1000 ml with distilled water, the amount titrated with sodium thiosulfate is only 1/50 the original concentration, and then the gram of "available chlorine" measured by titration must be corrected by a factor of 50.

$$\text{Volume percent} = \frac{(50)}{(10)}(\text{gms of available chlorine per liter})$$

The number of grams of available chlorine per liter, determined by titrating 25 ml of the diluted samples may be obtained from the preceding example for solid hypochlorites:

$$\text{(gms of available chlorine per liter)} = \frac{(0.1)(\text{ml } 0.1\text{N sodium thiosulfate})(35.46)}{25}$$

Substituting this equation in that for volume percent:

$$\text{Volume \%} = \frac{(50)}{(10)}\left[\frac{(0.1)}{(25)}(\text{ml } 0.1\text{N sodium thiosulfate})(35.46)\right]$$

$$= (0.7092)(\text{ml of } 0.1 \text{ sodium thiosulfate})$$

These tests are simple and relatively easy to carry out. The AWWA (1953) Standard for Hypochlorites likewise described the sampling and storage procedures for the hypochlorites.

APPENDIX F

DEVELOPMENT OF CHLORINE AS A DISINFECTANT

Sanitary wastes were being treated with chlorine (chloride of lime) around 1830. This was before the theory of spread of disease by microorganisms was put forth. It was being used with the belief that a reduction of the odors of sewage would also reduce disease. With this belief in mind and to control the odors of sewage in London, chlorinated lime was used in the first large plant treatment in 1854.

Through practice it was found that chlorinated lime would retard putrefaction of sewage and it was used to control septic conditions in surface waters receiving sewage.

Chlorination of typhoid wastes was begun in England in 1879 and in Hamburg, Germany, the first use for general disinfection of sewage took place in 1893. The following year disinfection of sewage using hypochlorites was being tried at Brest and Nice, France, Worthing England, and in Brewster, New York, sewage was being chlorinated to protect the water supply of New York City.

In the 1907 chlorination of sewage received its first serious consideration when E.B. Phelps conducted studies of disinfection with hypochlorite at the Red Bank, New Jersey Sewage Treatment Plant. This work was the impetus needed to expand the practice of sewage chlorination.

Liquid chlorine was put into use in the U.S. for disinfection of sewage in 1914. The success of the use of liquid chlorine caused many sewage treatment plants to begin disinfection by this method, Laubusch (1960b); Laubusch (1960c); Chamberlin (1948).

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